Selective Oxidation Processes

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Ellis K. Fields, *Symposium Chairman*

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FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are reviewed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications.

PREFACE

Huge volumes of chemicals are made by oxidizing selected fractions from petroleum. Much recent research has been concerned with extending the range, improving the selectivity, and determining the mechanisms of such reactions. The Petroleum Division, therefore, organized a Symposium on Selective Oxidation Processes for the 148th Meeting of the American Chemical Society at Chicago, September 3–4, 1964. This volume contains revised or expanded versions of 10 of the 15 papers presented at that symposium.

It has always been a fond hope of organic chemists to oxidize benzene directly to phenol. This has been achieved by several paths—irradiation of benzene in water or by oxidation in the vapor phase—but always in extremely low conversions. Chapter 1 demonstrates a method of hydroxylating selected aromatics in high yields. Chapter 2 also deals in hydroxylation of olefins by hydrogen peroxide.

Chapters 3 and 4 discuss vapor phase oxidations. In Chapter 3, fast flow pyrolysis of *p*-xylene involves *p*-methylbenzyl radicals as a common intermediate. The mechanism of allylic oxidation of isobutylene is of interest in its own right and sheds light on the mechanism for the industrial preparation of acrylonitrile from propylene, oxygen, and ammonia.

The next four chapters concern liquid phase oxidations. Three general methods for oxidizing aromatic hydrocarbons are represented by Chapters 5, 6, and 7. In Chapter 5 sulfur dioxide is used as the oxidant with a wide variety of substrates. Chapter 6, on the autoxidation of olefins, concerns a subject that has intrigued chemists since the researches of Farmer, Bawn, and Bateman and has contributed much to our understanding of the fundamental reactions of autoxidations of unsaturated materials ranging from simple olefins to rubbers and fats. Chapter 7, on the cleavage of tertiary alcohols by dichromate, brings in a relatively new effect of oxygen on the intermediate chromate esters. Chapter 8 describes the use of nitrogen dioxide catalyzed by selenium dioxide. This process and Amoco's liquid phase oxidation with air, using transition metal catalysts and a bromine initiator, are unusual in preserving the ring structure of alkylnaphthalenes and giving naphthalenecarboxylic acids.

Chapter 9 describes ozone as a selective oxidant used in the presence of a reactive nucleophile, hydrogen cyanide, to give cyanohydrins or aminonitriles directly from olefins.

The last chapter concerns another very active field in oxidation research—the oxidations of carbanions. These take place in solvents that form exceedingly strong hydrogen bonds and greatly enhance the strength of the bases by removing their solvent shells.

In view of the intense academic and industrial interest in oxidation processes, another such symposium will probably be forthcoming in the near future. Many advances are expected in mechanisms and synthesis. We hope that the first symposium will have served to prepare the way for some of the new research.

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Whiting, Ind.
November 1964

1

Oxidations with Peroxytrifluoracetic Acid-Boron Fluoride

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Peroxytrifluoroacetic acid-boron fluoride provides a potent, versatile, and selective oxidant, particularly for aromatic systems. The reagent can be thought of as a potential source of electrophilic hydroxyl, OH+. Three types of reaction are demonstrated: (a) electrophilic attack at an unsubstituted aromatic position, resulting in the direct introduction of a hydroxyl group, (b) attack at an already substituted ring position, followed by a Wagner-Meerwein rearrangement, leading to either a rearranged phenol or a 2,4-cyclohexadienone, and (c) hydride abstraction from a methyl group para to a phenolic hydroxyl, leading ultimately to diphenylmethane derivatives. Finally, the reagent smoothly converts tetramethylethylene to pinacolone. All of these reactions proceed well at —40° to 0° C.

For many reasons it is desirable to have reagents available which function as if they were sources of electrophilic or positive hydroxyl, abbreviated in this paper as OH^+. Were such reagents available, one could envision direct hydroxylation of aromatic compounds, electrophilic attack on double bonds leading to epoxides, to carbonyl compounds, to alcohols, or even to cationic polymerization initiated by OH^+, giving long-chain alcohols directly. The present paper describes some oxidations using peroxytrifluoroacetic acid-boron fluoride as a potent electrophilic oxidant; for convenience only, mechanisms will be written using OH^+ as the oxidant although it is recognized that this species is probably not the true oxidant (for example, the positive hydroxyl species may have trifluoroacetate or other ligands attached). Some of the reactions are certainly

unique and afford new products which otherwise would be difficult to obtain.

One can imagine that hydrogen peroxide, in strong acid, might be protonated and lead to a potent oxidant. The concentration of protonated

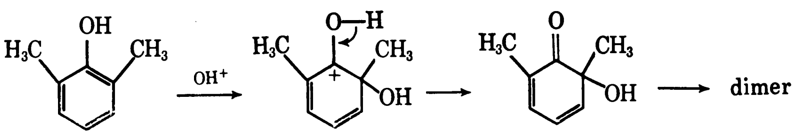
$$H{-}O{-}O{-}H \underset{}{\overset{H^+}{\rightleftharpoons}} H{-}\overset{H}{\underset{\oplus}{O}}{-}O{-}H \longrightarrow H_2O + OH^+ \quad (1)$$

peroxide is estimated to be about 1% in 10N acid. The hydroxyl cation, OH^+, was the assumed intermediate in the conversion of mesitylene to mesitol by hydrogen peroxide in acetic-sulfuric acid (3). A Lewis acid, boron fluoride-etherate, has been used in place of mineral acid with hydrogen peroxide to oxidize *m*-xylene, in low yield, to phenols and quinones (8).

Peroxytrifluoroacetic acid was considered to be an excellent source of positive hydroxyl because the trifluoroacetate ion is a good leaving group (2).

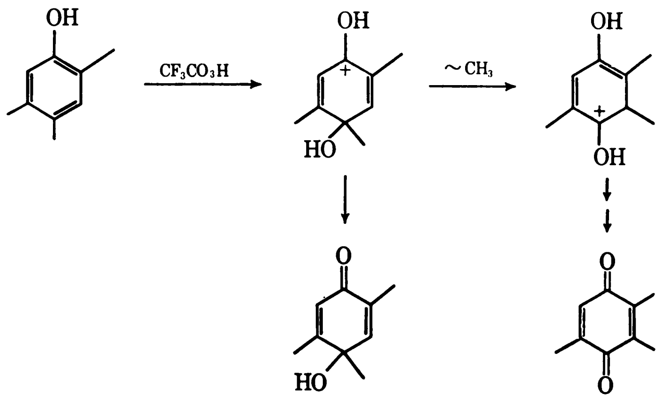
$$CF_3\overset{O}{\overset{\|}{C}}{-}O{-}O{-}H \longrightarrow CF_3CO_2^- + OH^+ \quad (2)$$

Using excess peracid, Musgrave *et al.* (2) obtained 30–40% conversions of alkylbenzenes to phenols and quinones. *m*-Xylene gave 2,4- and 2,6-xylenols; this orientation strongly suggests that the reaction involves hydroxyl cation rather than hydroxyl radical. The reaction has been extended by McClure (9) to the preparation of *o*- and *p*-methoxyphenols from anisole and analogous phenoxyphenols from diphenyl ether. The products from 2,6-xylenol and peroxytrifluoroacetic acid depend upon reaction conditions; either 2,6-dimethylbenzoquinone or 6-hydroxy-2,6-dimethyl-2,4-cyclohexadienone dimer may predominate, slow addition of the peroxide to the phenol favoring the latter (7). The dienone presumably arises by attack of OH^+ at one of the methyl-substituted positions:



(3)

Methyl migration, via a Wagner-Meerwein type rearrangement, has also been noted in a few instances (2). For example, oxidation of 2,4,5-trimethylphenol with peroxytrifluoroacetic acid at room temperature for 24 hours gave some trimethyl-benzoquinone, probably as shown:



(4)

A small yield of quinol was isolated, clearly showing attack by the oxidant at the substituted 4-position.

Although oxidations with peroxytrifluoroacetic acid seems to be useful (*2, 7, 9*), conversions are often low and the use of peracid is rather inefficient. It occurred to us that a Lewis acid might facilitate the decomposition of peroxytrifluoroacetic acid (Equation 2) through coordination with one of the oxygens not used ultimately as an oxidant.

Accordingly, the reagent, peroxytrifluoroacetic acid-boron fluoride, and several similar systems have been investigated as oxidants (*1, 5, 10*).

Experimental

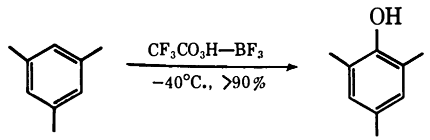
Mesitol from Mesitylene. A methylene chloride solution of peroxytrifluoroacetic acid was prepared by mixing 35 grams (0.167 mole) of trifluoroacetic anhydride, 50 ml. of methylene chloride, and 4 ml. (0.147 mole) of 90% hydrogen peroxide at 0° C., then allowing the solution to warm to room temperature for several minutes. This peracid solution, cooled to 0° C., was added dropwise to a solution of 56.1 grams (0.468 mole) of mesitylene in 100 ml. of methylene chloride, during which time boron fluoride (0.147 mole) was bubbled through the reaction mixture. The reaction was strongly exothermic, and the temperature was kept below 7° C. by a salt-ice bath (reaction proceeds well at temperatures as low as —40° C.). After addition was complete (2.5 hours) the solution was warmed to room temperature, hydrolyzed with 100 ml. of water, and worked up. We obtained 32.0 grams of recovered mesitylene and 17.7 grams (88%) of mesitol, m.p. 69–70° C. In other experiments, run at —40° C., the yield of mesitol was virtually quantitative.

Results and Discussion

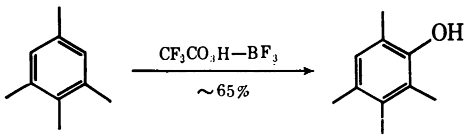
Addition of peroxytrifluoroacetic acid to a solution of excess mesitylene in methylene chloride, through which boron fluoride was passed, gave a nearly quantitative yield of mesitol, based on peracid used. The exo-

thermic reaction was run from —40° to 0° C. with external cooling. At higher temperatures further oxidation occurs, and the yield of mesitol decreases. The efficiency of the process, as measured by use of peracid, decreases markedly if the boron fluoride is omitted. The reaction occurs as rapidly as peracid is added; workup follows after 15 minutes stirring, following completion of the addition.

Isodurene is converted to isodurenol in 65% yield in a similar manner. In the latter case, other products, as yet uninvestigated, are formed.

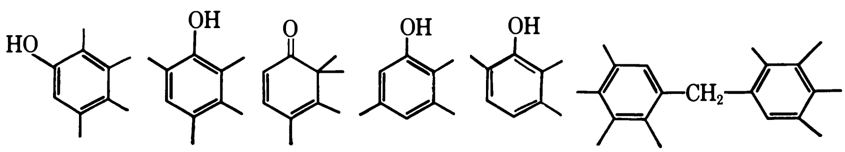


(5)



(6)

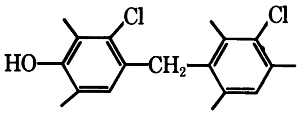
Extension of the reaction to prehnitene led to various products (II–VI) in addition to the expected prehnitol (I). Elucidation of the structures of these products led to some further understanding of the kinds of reactions CF_3CO_3H-BF_3 might induce and to unique dienone and other syntheses. The yields of I–VI from prehnitene and CF_3CO_3H,



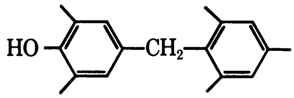
I II III IV V VI

with and without boron fluoride, are summarized in Table I. I is accounted for by ordinary electrophilic substitution at the vacant ring position. II and III presumably arise from electrophilic attack at C-1 followed by a methyl shift. IV–VI can be explained by hydride transfer from the para-methyl groups of I and II, followed by alkylations and debenzylations as shown in schemes 7 and 8.

Evidence that this mechanism can be correct in broad outlines was derived from an oxidation of chloromesitylene. Chloromesitylene was oxidized at 5°–7° C. with peroxytrifluoroacetic acid and boron fluoride in methylene chloride, using 2.4 moles of substrate per mole of oxidant. The oxidation was reasonably efficient, 0.85 moles of chloromesitylene being consumed per mole of peracid. Three crystalline products were isolated; the major one, formed in at least 39% yield, melted at 142.5–143.5° C. A detailed study of its NMR and mass spectrum suggested that it was VIII.



VIII

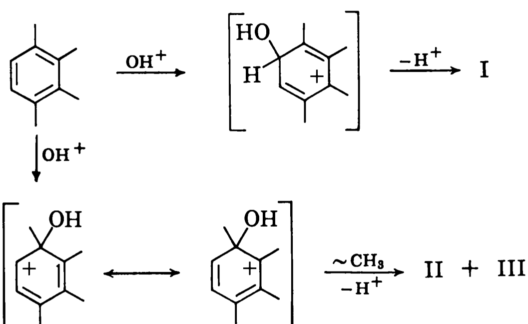


IX

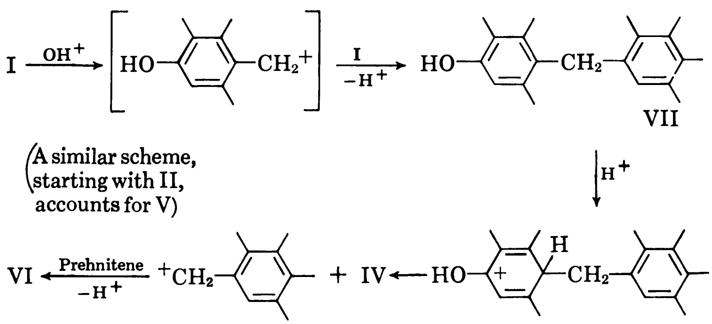
Table I. Summary of Oxidation of Prehnitene with CF_3CO_3H

	With BF_3		*Without BF_3*	
Prehnitene used (mmoles)	121.0		121.0	
Peracid used (mmoles)	38.3		38.3	
Prehnitene recovered (mmoles)	87.9		109.4	
Efficiency (prehnitene oxidized/peracid used), %	86.2		30.3	
Products	*Moles*	*% of Prehnitene Oxidized*	*Moles*	*% of Prehnitene Oxidized*
Prehnitol (I)	3.0	9.1	2.2	19.0
Isodurenol (II)	1.2	3.6	2.0	17.2
Cyclohexadienone (III)	0.58	1.8	1.1	9.5
Unknown, mass 182[a]	—	—	2.0	17.2
2,3,5-Trimethylphenol (IV)	4.8	14.5		
2,3,6-Trimethylphenol (V)	1.8	5.4	0.9	7.8
2,2',3,3',4,4',5,5'-Octamethyldiphenyl methane (VI)	3.9	23.6	(small)	
Total	15.3	58.0	8.2	70.7
Residue (grams)	1.2		0.8	

[a] This compound is tentatively assigned the structure 2,4-dihydroxy-3,4,5,6-tetramethyl-2,4-cyclohexadienone.



(7)

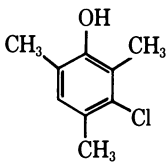


(8)

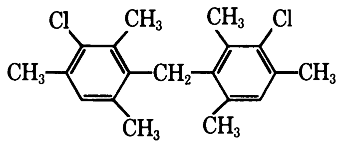
Postulated Mechanisms for Oxidation of Prehnitene

The structure was confirmed by reduction with lithium sand to IX, m.p. 121°–123° C., an authentic sample of which was synthesized from chloromethylmesitylene and 2,6-xylenol. It will be noted that VIII corresponds in structure to compound VII in the proposed oxidation scheme for prehnitene.

The other two oxidation products of chloromesitylene were isolated pure in approximately 10% yield each. One of these, m.p. 83°–84° C., was identical (IR, NMR) with a sample of 3-chloromesitol (X) prepared by careful chlorination of mesitol. The other, white prisms melting at 118°–119° C., is assigned structure XI on the basis of elemental analysis and NMR spectrum (sharp singlets at 7.96, 7.85, 7.75, 5.97, and 3.21 with relative areas 3:3:3:1:1). Compound XI corresponds to compound VI



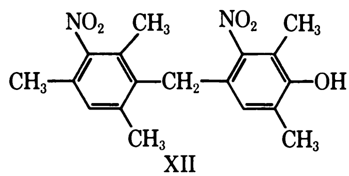
X



XI

in the prehnitene oxidation. Debenzylation is less important in the chloromesitylene oxidation than in the prehnitene oxidation (—i.e., VIII is less readily debenzylated than VII) probably because of the destabilizing influence of the chloro substituent on the intermediate benzyl cation.

Nitromesitylene, oxidized using an excess of aromatic, gave only a single crystalline product, m.p. 244°–245° C., in 21% yield. The product is assigned structure XII based on analysis, infrared and NMR spectra, and analogy with VIII. The low recovery of pure, unreacted nitromesitylene (only about 60% of theory) and formation of considerable amounts of intractable tar suggest that the strongly electron-withdrawing nitro group inhibits the normal electrophilic substitution by OH^+ and favors side reactions.



XII

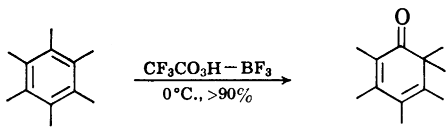
At this point then, one can summarize that three types of reactions have been demonstrated for the reagent CF_3CO_3H-BF_3:

(a) Electrophilic attack at an unsubstituted aromatic position resulting in the direct introduction of a hydroxyl group.

(b) Attack at already substituted ring position, followed by a Wagner-Meerwein rearrangement, leading to either a rearranged phenol or a 2,4-cyclohexadienone.

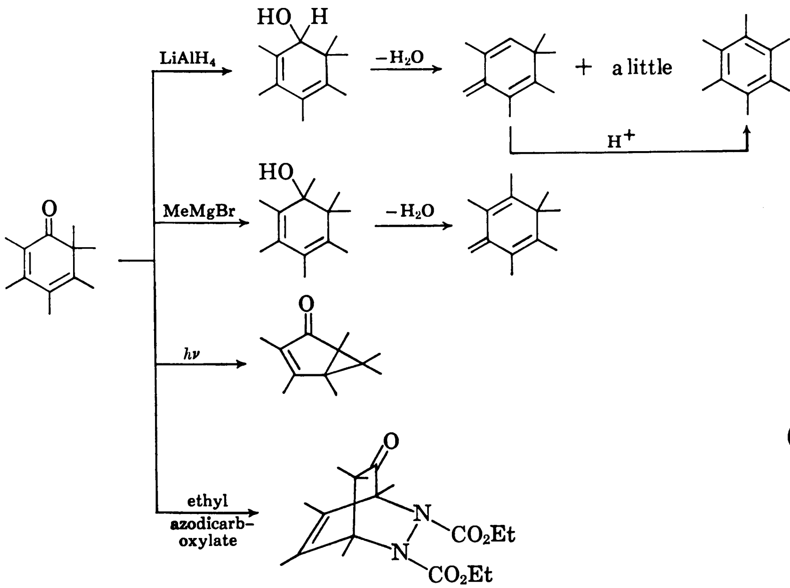
(c) Hydride abstraction from a methyl group para to a hydroxyl group, leading ultimately to diphenylmethane derivatives.

It seemed particularly desirable to exploit the dienone synthesis further. Emboldened by the recovery of cyclohexadienone III from the oxidation of prehnitene, albeit in low yield, we applied the reagent to hexamethylbenzene hoping that dienone would be the major product. These efforts were rewarded since the oxidation of hexamethylbenzene with CF_3CO_3H-BF_3 at 0° C. gave the crystalline dienone XIII (m.p. about room temperature) in over 90% yield. The structure of XIII was demon-



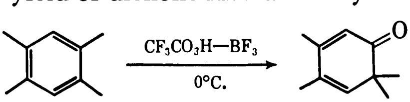
XIII (9)

strated by its elemental analysis, spectra, and chemical conversions, some of which are shown in Scheme 10.



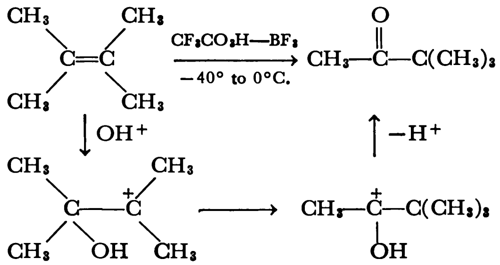
(10)

Hexaethylbenzene is similarly oxidized in high yield to hexaethyl-2,4-cyclohexadienone. Surprisingly, the major products from the oxidation of pentamethylbenzene are dienones, no pentamethylphenol being detected by gas chromatography. Even the oxidation of durene with CH_3CO_3H-BF_3 gave over 50% yield of dienone XIV and very little duroquinone (*6*).



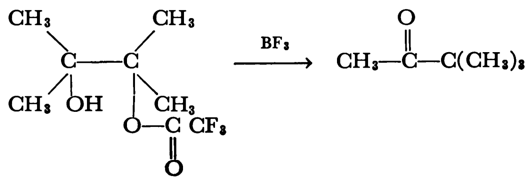
XIV (11)

Finally, the intermediate envisioned when one adds OH^+ to a tetra substituted olefin resembles closely the intermediate cation in the pinacol-pinacolone rearrangement. It seemed desirable, therefore, to carry out an oxidation of tetramethylethylene with $CF_3CO_3H\text{-}BF_3$. When this was done, at —40° C. in methylene chloride as solvent, a nearly quantitative yield of pinacolone was obtained.



(12)

When BF_3 was omitted, the yield of pinacolone was reduced to 16%, and the major product was the hydroxy-trifluoroacetate XV which on treatment with boron fluoride gave pinacolone quantitatively.



(13)

XV

From these results, it is clear that peroxytrifluoroacetic acid-boron fluoride is an extremely potent oxidant capable of various highly selective, unique, and useful oxidations, and its use in synthesis is being investigated further. The experimental details of these oxidations will be presented elsewhere, but a typical oxidation of mesitylene to mesitol is given here to illustrate the general procedure used.

Acknowledgment

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2

Hydrogen Peroxide Reactions with Olefins

Reinvestigations of the Milas Reaction

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The osmium tetroxide-catalyzed addition of hydrogen peroxide to olefins has been reinvestigated with innovations of reagents, catalyst, and procedures to obtain product analyses and material balances for the hydrogen peroxide consumption. Significant amounts of carbonyl by-products—acetol, organic acids, peracids, and possibly pyruvaldehyde—are formed under the range of conditions studied. Experimental design studies of the effects of reaction variables upon yields of the various products under batch and continuous addition conditions have been completed. The nature of the catalytic complex involved in the initiation of the reaction is reviewed. The order and rate of product appearance does not support a simple oxidation sequence. A branching reaction sequence consistent with experimental results is proposed.

Hydrogen peroxide is becoming less expensive and has been used for the liquid-phase oxidation of olefins (*7, 21, 22, 23, 24, 26, 34, 38, 39*); but its use in oxidizing gaseous olefins has not received much attention. We have investigated its use in oxidizing gaseous olefins, especially propylene, noting in particular the glycol and by-product yields obtained.

A review of the chemical literature (*1, 2, 5, 16, 20, 30, 40*) and laboratory experiments confirmed that the Milas reagent (*14, 19, 21, 22, 23, 24, 26, 28*), osmium tetroxide in *tert*-butyl alcohol, is one of the more effective catalysts for liquid-phase oxidation.

$$R_1—CH{=}CHR_2 + H_2O_2 \xrightarrow[\text{trace } OsO_4,\ 0° C.]{tert\text{-}BuOH} R_1—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—R_2 \qquad (1)$$

We found, however, that actual glycol yields from gaseous olefins were not as high with this reagent as reported in the literature (*26*), and that considerable amounts of more highly oxidized by-products were also obtained. We have investigated some of these by-products, established their identities, excluded some possible by-products, and determined the reaction conditions which favor their formation. We devoted special attention to the by-products from propylene, especially acetol, a potential petrochemical.

Experimental

Apparatus. The reaction of hydrogen peroxide in *tert*-butyl alcohol with liquid olefins can be carried out in glass flasks equipped with cooling and condensing facilities. The reaction of gaseous olefins is more difficult: either the gas must be entrained through the reagent (*22*), or its solubility must be increased by pressure.

A Parr hydrogenation apparatus (*27*) with a glass bottle was found suitable for propylene reactions at low pressures. Later, we modified the system by adding an external, copper water coil for isothermal control, a tube connected to a syringe or a Lapp pump for continuous reagent addition, a glass thermocouple well, and a sample withdrawal tube (Figure 1).

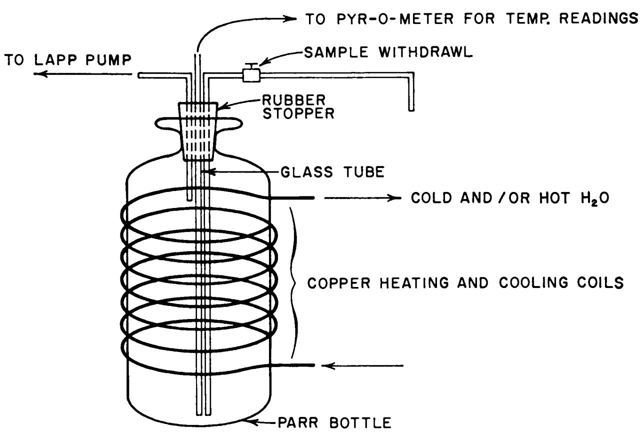


Figure 1. Modified Parr apparatus

Preliminary kinetic studies were run in a glass buret system which was convenient for studying reactions at atmospheric pressure and allowed periodic withdrawal of samples for analysis. Subsequent kinetic studies were carried out in the Parr apparatus and in sealed ampoules.

Two F&M programmed temperature gas-liquid chromatographs, Models 500 and 720, were used to analyze reaction mixtures. A Perkin-Elmer Model 21 infrared spectrophotometer, a Cary Model 14M recording spectrophotometer, and a Zeiss refractometer were used to confirm products and product derivatives and to study intermediate reaction complexes. Ultraviolet spectra were run in 1 cm. quartz cells using pure *tert*-butyl alcohol as blank solvent.

Reagents and Procedures. Reagents used were of the best purity commercially available. Most of the work was done with propylene although other olefins were used to determine the scope and generality of the reaction.

Hydrogen peroxide solutions were prepared either by Milas' procedure (*21*) or more directly by dilution of Becco 98% hydrogen peroxide reagent. The latter procedure is more convenient for preparing a dry reagent.

Special safety precautions were observed in handling the osmium tetroxide (*32*) and the 30 and 98% solutions of hydrogen peroxide (*8, 9, 10, 11*) which presented no difficulty.

Acid-base titrations were made with standardized 0.1*N* hydrochloric acid. Periodic acid titration was used to determine the combined α-dioxygenated product yield in the reaction mixtures (*17, 25, 31, 33*). We adopted an iodometric method modified to distinguish between hydrogen peroxide and peracids based on a two-step titration with ceric sulfate solution and standard sodium thiosulfate solution (*13*). Dialkyl peroxides do not react with iodine under these conditions (*3, 18*).

2,4-Dinitrophenylhydrazine, *o*-phenylenediamine, and semicarbazidehydrochloride reagents (*35*) were used to make derivatives of carbonyl compounds in the reaction mixtures. Dinitrophenylhydrazones were isolated, purified, and identified by melting point and infrared spectra. Semicarbazones were characterized in the same manner and by carbon, hydrogen, and nitrogen analyses.

The presence of carbonyls was also confirmed by infrared spectra of the reaction mixtures. Chromatography (*15, 37, 43*) and infrared spectra of derivatives (*41*) can be used to identify reaction products, but results are complicated by the fact that glycols (*42*) and α-hydroxyketones (*29*), under certain conditions, may be oxidized to ketone derivatives by 2,4-dinitrophenylhydrazine. A typical run is described below.

To 50 ml. of a 2*M* hydrogen peroxide solution in an organic solvent (usually *tert*-butyl alcohol) in a Parr bottle was added 5 ml. of 0.5 wt.% osmium tetroxide in solvent. The bottle was installed, heated to temperature (usually in the range of 0°–80° C.), and contacted with propylene. The shaker was started. The exothermic reaction (Figure 2) proceeded with the solution changing from reddish-brown to clear on formation of the oxidation products, and to a final brown color. After 30 minutes, the reactor was stopped and evacuated of propylene.

Toward the end of the reaction, the reddish-brown soluble complex changed to a clear and then dark brown-to-black colloidal suspension. Reaction product mixtures which had turned black contained only traces of residual hydrogen peroxide. After reaction, a propylene pressure drop of several pounds was observed for the 3-liter gas volume of the Parr apparatus system. The reaction mixture was degassed of dissolved pro-

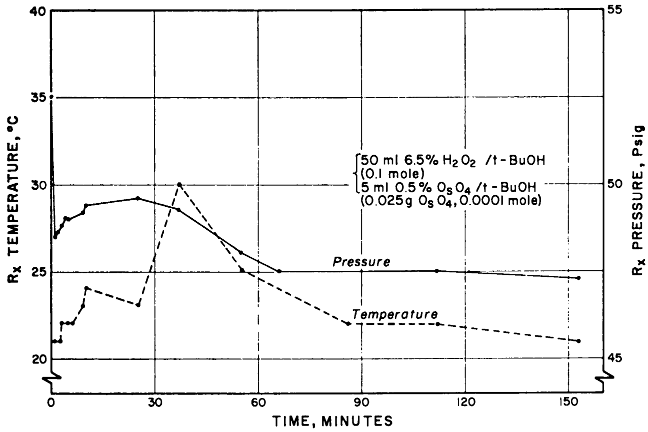


Figure 2. Reaction of propylene with hydrogen peroxide

pylene by applying house vacuum, and a volume and weight increase of about 1–2% was observed.

The reaction product mixtures were analyzed by the following methods:

a. Residual hydrogen peroxide by titration with ceric sulfate (*13*).
b. Total α-dioxygenated products by titration with periodic acid.
c. Peracids by sodium thiosulfate titration (*4*).
d. Organic acids by titration with a standard base.
e. Carbon dioxide by nitrogen entrainment of the gas phase through sodium hydroxide solution, precipitation with barium chloride, and weighing as barium carbonate.

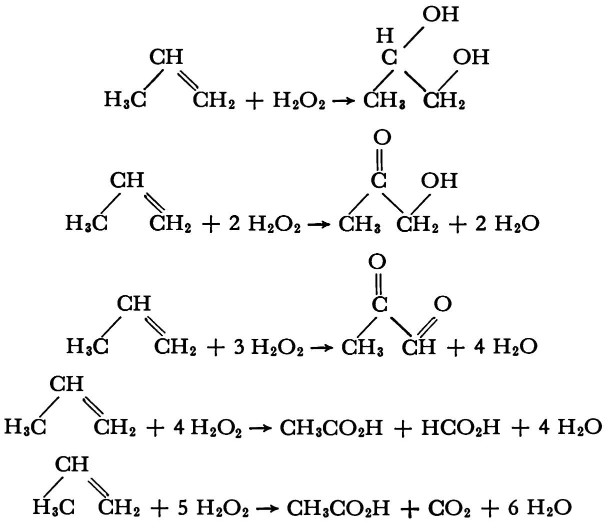
Gas-liquid chromatography was performed on the gaseous reaction phase for oxygen, nitrogen, ethane, carbon monoxide, carbon dioxide, and propylene using an F&M Model 300 gas-liquid chromatograph equipped with a 2-ft. column packed with 13X molecular sieves.

The liquid product phase was analyzed by gas-liquid chromatography for *tert*-butyl alcohol, water, acetol, acetic acid, pyruvaldehyde, and propylene glycol using F&M Model 500 and 720 gas-liquid chromatographs and helium carrier gas.

Calculations. The calculations based upon titrametric measurements are straightforward. Gas chromatogram peak areas were approximately proportional to the weight percents of components in the mixtures, but greater precision was obtained by using standard calibration mixtures similar to the types of product mixtures being analyzed. From the analyses and the reaction stoichiometries, the material balances were calculated.

Because hydrogen peroxide is more expensive than most olefins, for practical considerations we based our yields on this reagent and employed excess olefin. The stoichiometries assumed for the reaction products detected from the propylene reaction are given below.

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2 \qquad (2)$$



(3)

(4)

(5)

(6)

(7)

Hydrogen peroxide material balances for two runs, using the stoichiometries of Equations 2 through 7, are summarized in Table I. About 80% of the original hydrogen peroxide is accounted for; the remaining 20% is probably consumed to produce small amounts of more highly oxidized reaction products which were not detected.

Table I. Hydrogen Peroxide Material Balance for Oxidation of Propylene

	Moles H_2O_2	
Input:	0.1325	0.1325
Accounted for:		
Residual H_2O_2 at end of run	0.0003	0.0003
Reaction Products:		
Propylene glycol	0.0391	0.0389
Acetol	0.0224	0.0224
Pyruvaldehyde	0.0025	0.0025
Free organic acids	0.0130	0.0124
Organic peracids	0.0068	0.0050
Carbon dioxide	0.0045	0.0045
Oxygen	0.0162	0.0162
Drainage loss (2%)	0.0018	0.0018
Total mole H_2O_2	0.1086	0.1040
% H_2O_2 accounted for	80.5	78.5

Results and Discussions

Various solvents were tested for their stability toward hydrogen peroxide in the presence or absence of osmium tetroxide catalyst (Table II). We observed that hydrogen peroxide is stable in *tert*-butyl alcohol and *tert*-amyl alcohol for several months at room temperature and for several days at 50°C. However, secondary and primary alcohols are slowly attacked at 50°C. 1,2-Glycols are only slowly oxidized under the reaction condition but not sufficiently to account for the major proportions

of the oxidation by-products obtained from olefins. Hence, because of their demonstrated stability under the reaction conditions, tertiary alcohol solvents were used for most of the experiments.

Table II. Stabilities of Various Materials to Milas Reagent[1]

	DNP Test at 23°C. and 24 Hr.[3]	*DNP Test at 50°C. and 72 Hr.*[3]
Alcohols		
Methanol	—	+
Ethanol	—	+
2-Propanol	—	+
n-Butyl Alcohol	—	+
Isobutyl Alcohol	—	++
tert-Butyl Alcohol	—	—
tert-Amyl Alcohol	—	—
Iso-Octyl Alcohol[2]	—	—
Miscellaneous		
Allyl Alcohol	++	not run
Ethylene Glycol	+	+++
1,2-Propanediol	+	+++
1,3-Propanediol	—	not run
Glycerol	++	++
Sorbitol	+	++
Glycolic Acid	–	–
γ-Butyrolactone	not run	–

Hydrogen peroxide in *tert*-butyl alcohol.
Primarily isomeric primary alcohols.
Key: (—) Negative; (+) Positive; (++) Very Positive; (+++) Strongly Positive.

In agreement with Milas' and Mudgan's findings, we found osmium tetroxide the most effective catalyst for reaction with propylene. Catalyst solutions of osmium tetroxide in tertiary alcohols discolor within a few hours, but these discolored solutions are only slightly less active than freshly prepared solutions, and only a trace of hydrogen peroxide is needed to reoxidize the lower valence osmium oxide to a soluble, colorless catalytic form in the solution. Powdered osmium metal is not oxidized by hydrogen peroxide under the reaction conditions and does not function as a catalyst.

Hydrogen peroxide is fairly stable to either the catalyst or the olefin alone for periods of an hour or so, but vigorous exothermic reaction occurs when all three reactants are present.

The reaction with gaseous olefins is very pressure sensitive. The rate of reaction, as evidenced by hydrogen peroxide disappearance and pressure drop, is very slow at atmospheric pressure. (No color complex or exotherm was observed with propylene at pressures below 20 p.s.i.g., but at 25–50 p.s.i.g. the reaction with propylene was characterized by the rapid formation of a bright reddish-brown complex, with pronounced heat effect within one minute after admission of the olefin.)

Strong dinitrophenylhydrazone (DNP) precipitates were obtained with all gaseous and liquid olefins tested in Table III.

Table III. Evidence for Carbonyl Derivatives from Olefin Reactions with Milas Reagent[1]

	Conditions		
Olefin	*Temp., ° C.*	*Time, Hr.*	*DNP Test[a]*
Propene	20–40	1/2	+++
trans-Butene-2	20–Reflux	1/2	+++
Pentene-1	20–Reflux	1/2	+++
Pentene-2	20–Reflux	1/2	+++
2-Methylbutene-1	20–Reflux	1/2	+
2-Methylbutene-2	20–Reflux	1/2	+
cis-4-Methylpentene-2	20–Reflux	1/2	++
trans-4-Methylpentene-2	20–Reflux	1/2	+++
Hexene-2	20–Reflux	1/2	+++
Cyclohexene	20–Reflux	1/2	++
Heptene-3	20–Reflux	1/2	++
Octene-2	20–Reflux	1/2	++
2,4,4-Trimethylpentene-2	20–Reflux	1/2	++
2,6-Dimethylheptene-3	20–Reflux	1/2	++
2-Butyne	50	72	+++
Styrene	20–Reflux	1/2	+++
cis-Stilbene	20–Reflux	1/2	+++
trans-Stilbene	20–Reflux	1/2	+++

Infrared spectra of product mixtures all show strong carbonyl absorption in the region 5.75–6.1.
Key: (—) Negative; (+) Positive; (++) Very Positive; (+++) Strongly Positive.

Product Analyses. The propylene reaction mixture had a pronounced odor reminiscent of low-boiling carbonyl derivatives. A positive periodic acid test (*36*) indicated the presence of one or more of the following products: glycol, α-hydroxycarbonyls, α-dicarbonyls. Infrared inspection of the product mixture confirmed the presence of several types of carbonyl groups, showing strong absorption in the infrared at 5.8 μ and 6.0–6.1 μ (Figure 3). An instant strong positive test with dinitrophenylhydrazine reagent indicated the presence of aldehydes and/or ketones. A strong acidic reaction with moist pH paper (pH ~3) indicated the presence of acidic material.

Gas-liquid chromatographic inspection of the gas phase from a propylene reaction mixture showed small amounts of oxygen, owing to some

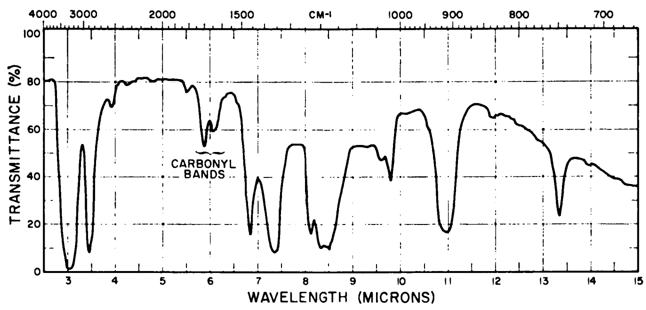


Figure 3. Infrared spectrum of reaction product solution from propylene-hydrogen peroxide reaction shows two carbonyl bands

hydrogen peroxide decomposition, and small amounts of carbon dioxide from the further known oxidation of some of the organic acids (*12*). The oxygen produced by hydrogen peroxide decomposition was calculated from the gas chromatogram area after subtracting an original air-oxygen value (determined by multiplying the nitrogen content by the atmospheric oxygen-to-nitrogen ratio of 1:4).

The gas-liquid chromatogram of the gas atmosphere showed no carbon monoxide or formaldehyde present, nor did entraining the gas phase in a nitrogen purge stream through dinitrophenylhydrazine reagent give a positive test for either formaldehyde or acetaldehyde. Acetaldehyde was shown to be fairly stable to the reaction conditions for one hour at 50°C. and to give a very strong positive dinitrophenylhydrazone test by this entrainment procedure. Therefore, the production of volatile aldehydes, such as formaldehyde and acetaldehyde, as reaction intermediates and by-products from propylene was ruled out.

Propylene glycol was confirmed and determined by calibrated gas-liquid chromatographic analysis of reaction product mixtures against similar concentrations of authentic 1,2-propanediol. Periodic acid titration values were higher than the gas-liquid chromatography values for propylene glycol, but agreed closely with the combined gas-liquid chromatography values for glycol, acetol, and pyruvaldehyde.

Acetol was identified by comparing gas-liquid chromatographs and infrared spectra with those of authentic acetol samples and by isolation via distilling (42°–46°C./32 mm., corrected to 140°–145°C./760 mm.; literature—146°C./760 mm.).

A dinitrophenylhydrazine test for pyruvaldehyde gave a derivative whose melting point (298°–302°C.; authentic sample—302°C.) and infrared spectrum were in agreement with authentic pyruvaldehyde dinitrophenylhydrazone derivative. (We were unable to prepare an *o*-phenylenediamine derivative of pyruvaldehyde from the reaction mixture.)

Elution chromatography of the crude reaction product DNP over alumina with ether-petroleum ether eluant gave a yellow and an orange zone on the column indicating at least two carbonyl derivatives. The orange DNP was shown to be derived from pyruvaldehyde; the yellow one was not isolated, but was presumed to be that derived from acetol. Propylene glycol is not oxidized by dinitrophenylhydrazine under the conditions used. But acetol is readily oxidized by dinitrophenylhydrazine, and at least some pyruvaldehyde dinitrophenylhydrazone may have been formed by the oxidation of acetol by dinitrophenylhydrazine (*29*).

Direct gas-liquid chromatographic analysis of reaction mixtures containing pyruvaldehyde was complicated because acetic acid has the same retention time as pyruvaldehyde and was not separated from the latter under the column operating conditions. However, the peak obtained was

larger than that calculated for acetic acid by titration with standard sodium hydroxide. By subtracting the acetic acid value obtained by titration, the pyruvaldehyde content could be estimated. Gas-liquid chromatographic analysis indicated that small amounts of pyruvaldehyde survived the reaction conditions, although kinetic studies showed that pyruvaldehyde is readily oxidized by hydrogen peroxide under the conditions. Apparently, small amounts of pyruvaldehyde survived after the hydrogen peroxide was exhausted.

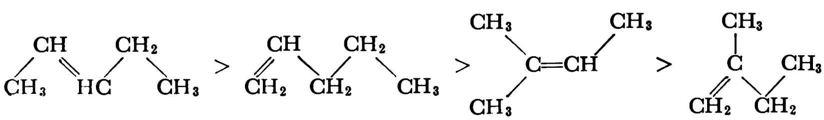
Peracids resulted from the well-known equilibrium reaction of organic acids with excess hydrogen peroxide (*38*), but their yields were low.

Most of the product organic acids remained as such in the reaction product mixture but were readily removed as sodium salts by extracting with aqueous sodium hydroxide. The sodium salts were recovered by rinsing the aqueous phase with ether to remove traces of other organic materials and evaporating the aqueous phase to dryness. Rinsing the dried salt with alcohol removed traces of glycol to yield a dried sodium salt mixture with an infrared spectrum identical to that of a 50-50 synthetic mixture of sodium acetate and sodium formate. This product salt mixture lacked the distinctive absorption bands unique for sodium oxalate and sodium pyruvate. Oxalic acid as a reaction product was also ruled out by a negative reaction with calcium ion.

Effect of Reaction Variables on Propylene Oxidation. The Parr apparatus was equipped with a temperature controller, and a series of experiments was completed to study the influence of some of the major reaction variables. In Figure 4 results are plotted against the major variables of an experimental design embracing temperature, propylene pressure, and hydrogen peroxide concentration. Similar mixtures were obtained over the temperature range 20°–80°C.; however, larger proportions of by-products were observed at the more severe reaction conditions. Greater selectivity toward acetol production and higher-efficiency hydrogen peroxide consumptions are obtained at higher temperatures, moderate-to-high propylene pressures, and lower hydrogen peroxide concentrations.

A continuous addition procedure allowed us to obtain good acetol yields at much higher concentrations of hydrogen peroxide than had been obtained or indicated in the batch experiments.

Effect of Olefin Structure. The effect of chemical structure upon exothermicity for a series of isomeric pentenes studied under identical conditions is shown in Figure 5. The order of observed exothermicities is shown below.



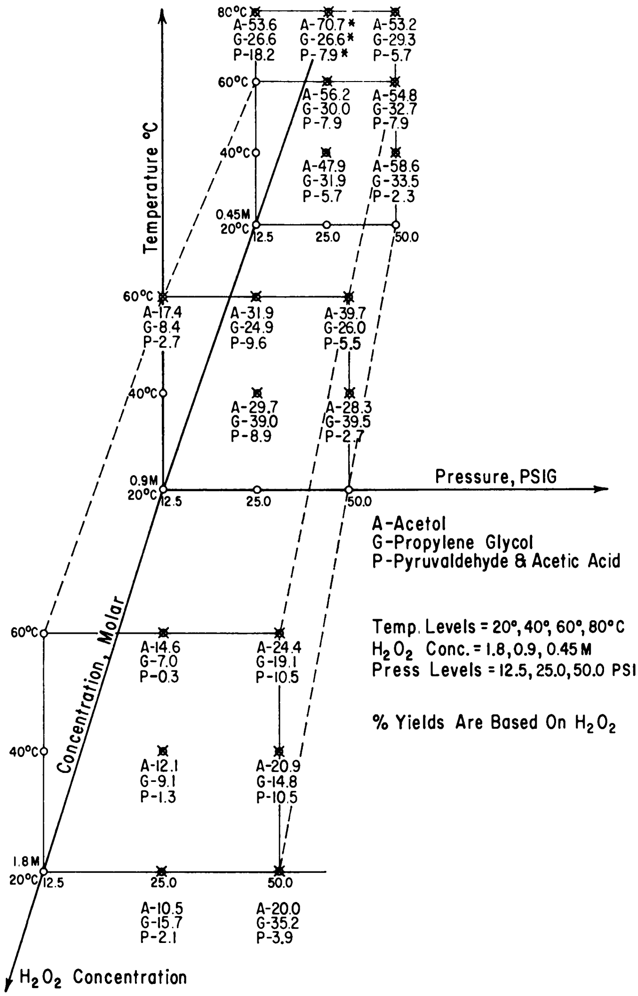


Figure 4. Effect of temperature, pressure, and concentration variables on the reaction of propylene with hydrogen peroxide

This indicates that the olefin exothermicity is affected by the alkyl-substitution of the double bond and suggests that both electronic (inductive and hyperconjugative) and steric factors may be operative.

The exothermicity order, pentene-2 > pentene-1, is reversed for the order of specific reaction rates observed for reaction with peracetic acid in acetic acid solution (*38*). In the latter reaction, it has been demonstrated that terminal olefins are very sluggish and internal olefins are more reactive.

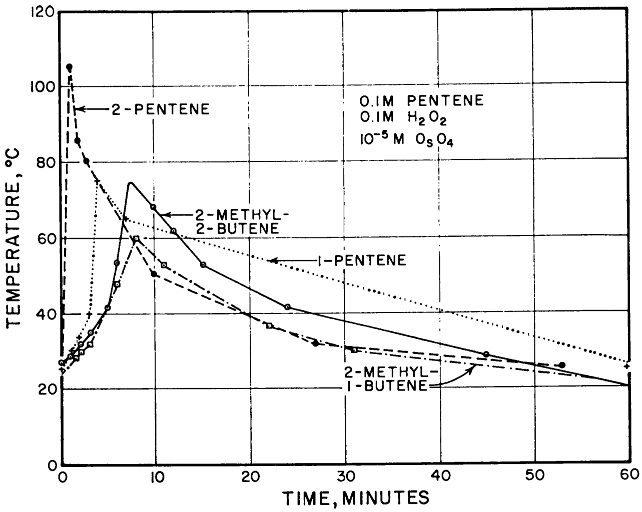


Figure 5. Reactivity of pentene isomers with H_2O_2/ iso-$C_8H_{17}OH$

Theoretical Discussions. EVIDENCE FOR AN OSMIUM COMPLEX. The reaction of osmium tetroxide with olefins is believed to proceed via an osmic ester complex which has been postulated as an initial intermediate in the reaction (*44*). Recently, Milas (*24*) summarized his investigations of this alleged osmic ester complex:

The hydroxylation of trimethylethylene and cyclohexene in *tert*-butyl alcohol with hydrogen peroxide in the presence of osmium tetroxide as catalyst has been studied spectroscopically. It has been found that the maximum absorption band due to osmium tetroxide-hydrogen peroxide in *tert*-butyl alcohol shifted during hydroxylation from 244 to 286 mμ with trimethylethylene and 288 mμ with cyclohexene. These maxima were also observed to occur when osmium tetroxide was allowed to react in *tert*-butyl alcohol with vicinal glycols in the absence of hydrogen peroxide. In the presence of excess hydrogen peroxide, these maxima shifted back to the maximum of osmium tetroxide–hydrogen peroxide mixture. It has been concluded that the maxima at 286 to 288 mμ are caused by complexes between osmium tetroxide and the glycols.

Figure 6 shows the ultraviolet spectrum of a freshly prepared solution of 1.9×10^{-4} *M* osmium tetroxide in *tert*-butyl alcohol purified by Milas' procedure (*24*). The clear solution and spectrum were stable for several hours, but the solution darkened after several days. It is noteworthy that the maximum at 244 mμ attributed to "osmium tetroxide-hydrogen peroxide" is present in fresh osmium tetroxide solution without hydrogen peroxide. Therefore, the 244 mμ maximum is no evidence for the osmium tetroxide-hydrogen peroxide complex or peroxyosmic acid. We were unable to get unambiguous ultraviolet evidence for the formation of an

osmic ester intermediate in osmium tetroxide-catalyzed hydroxylation of olefins with hydrogen peroxide.

Infrared investigations do not give any positive evidence of a characteristic ester-type complex between osmium tetroxide and olefin. Osmium tetroxide reacts explosively with liquid olefins. Spectra were obtained for solutions in *p*-dioxane and in *tert*-butyl alcohol, with a band ascribable to osmium tetroxide at 10.50–10.55 μ. This band disappeared, and two new bands appeared at 10.12 μ and 10.42–10.45 μ when osmium tetroxide and cyclohexene in solution were mixed in mole ratios of 1:3. Free olefin absorption at 13.95 μ was absent from this latter spectrum. This observation suggests that the complex incorporates more than one mole of olefin per mole of osmium tetroxide.

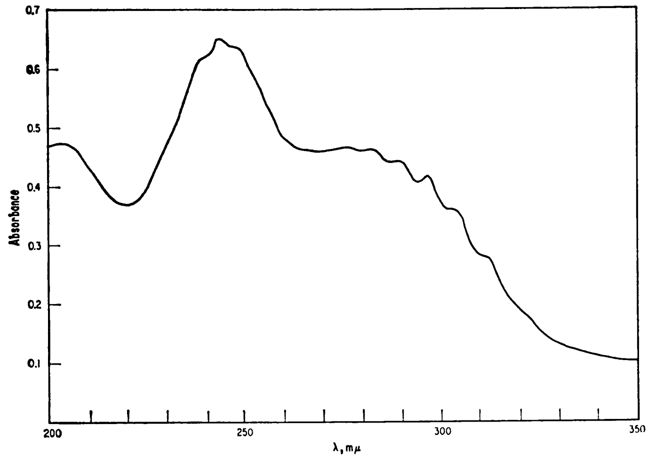


Figure 6. Ultraviolet absorption spectrum of fresh 1.9 × 10⁻⁴M OsO₄ in purified tert-butyl alcohol

Kinetic Evidence. Kinetic experiments were made in the Parr apparatus, and the product mixtures were analyzed for relative portions of acetol, acetic acid, pyruvaldehyde, and glycol. These results are summarized in Figure 7. Acetol is one of the first products appearing in the reaction mixtures under batch or continuous addition conditions. The acetol appears before the glycol and continues to build up during the oxidation. If the acetol were formed as a sequential product from the glycol, its maximum concentration should occur after the appearance of glycol.

The relative stabilities of the various reaction products were also studied. Convenient concentrations of the substrates were dissolved in the Milas reagent and sealed in glass ampoules which were thermostated and opened after various lengths of time for analysis. The relative order of stabilities shown in Table IV is: glycol $\gg$ acetol $>$ pyruvaldehyde.

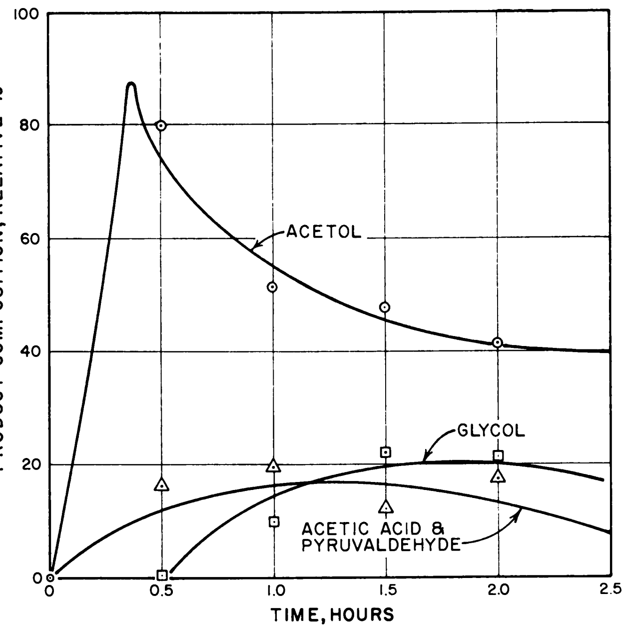


Figure 7. Order of appearances and relative amounts of reaction products disprove a single sequential oxidation mechanism

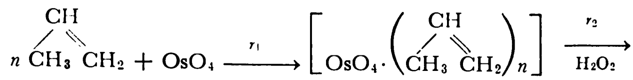
Conditions: reaction in Parr vessel with 50 ml. of 1.8M H_2O_2, 5 ml. 0.5% OsO_4, 5.0 p.s.i.g. propylene ot 20°C. with 1 gram KH_2PO_4 added as buffer

This order of relative stability does not support a sequential oxidation mechanism either. If the acetol were formed from the glycol, its maximum concentration would appear after that of the glycol, and since it is more readily oxidized than the glycol, it would disappear faster than it was formed and consequently would not be observed as an intermediate or product. This would be even more the case for pyruvaldehyde.

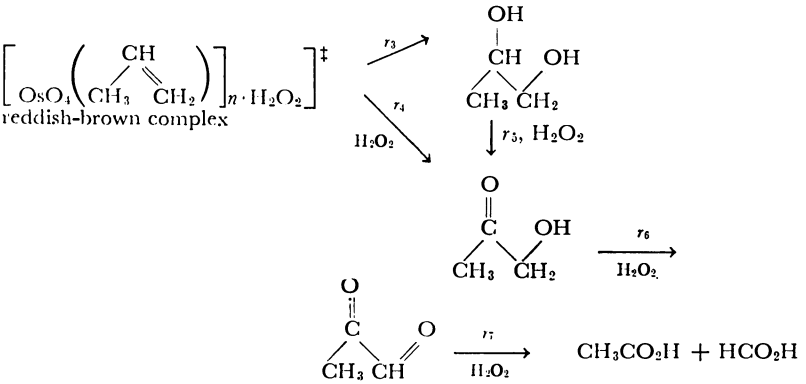
Table IV. Stabilities of Various Reaction Intermediates to Hydrogen Peroxide

Temperature, ° C.	*Substrate*	*Time for Half-Reaction (Sec. × 10^{-3})*
80	Propylene glycol	19
70	Propylene glycol	32
70	Propylene glycol (with added water)	36
60	Propylene glycol	100
60	Propylene glycol (with added water)	122
60	Acetol	11
60	Pyruvaldehyde	0.3

Proposed Reaction Mechanism. A proposed reaction mechanism consistent with experimental facts is outlined below.



(8)

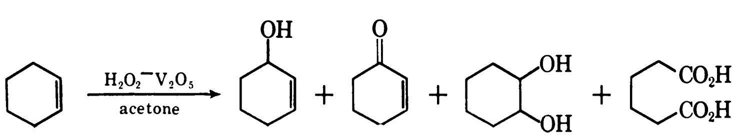


(9)

where $r_1, r_2 \gg (r_4 > r_3) > r_5$, and $r_7 \gg r_6$.

As indicated in Equation 8, the osmium tetroxide may react with more than one mole of olefin to form a brown complex characterized in the infrared by the disappearance of a unique osmium tetroxide band at 10.50–10.55 μ, the simultaneous disappearance of the olefinic cis-double bond band at about 13.95 μ, and the appearance of two new bands at 10.12 and 10.42–10.45 μ. This brown complex reacts rapidly with hydrogen peroxide to give the more highly colored, reddish-brown solution which is probably the catalytic peroxide complex. This complex decomposes to give propylene glycol which is one of the more stable products under the reaction conditions. Alternatively, a portion of the complex must react at a faster rate with another molecule of hydrogen peroxide to produce acetol, a less stable material under the conditions. (A small amount of the acetol may also be produced by the further oxidation of the glycol.) Subsequently, some of the acetol further oxidizes to the even less stable pyruvaldehyde intermediate, most of which is rapidly oxidized by another mole of H_2O_2 to yield acetic and formic acids. Some of the latter is further oxidized to carbon dioxide. There is no evidence for the formation of formaldehyde, acetaldehyde, pyruvic acid, oxalic acid, or carbon monoxide as reaction intermediates or products.

Our results may be contrasted with those reported by Eisenbraun and Bader (*6*) on the allylic oxidation of cyclohexene with hydrogen peroxide in acetone with vanadium pentoxide catalyst.



On analyzing their product mixture, they found, in addition to the anticipated glycol, significant amounts of 2-cyclohexene-1-ol and 2-cyclohexenone. We have found no evidence for allyl alcohol or acrolein in our reaction product mixture. In agreement with their work, however, we found no cleavage aldehydes, but rather acids as cleavage products.

Summary

The reaction of hydrogen peroxide with olefins is complicated by the formation of substantial amounts of carbonyl by-products, along with glycol, over the whole range of conditions studied. We investigated the reaction of propylene with hydrogen peroxide, analyzed the product mixtures, and determined the material balances for the hydrogen peroxide consumed.

An experimental design, carried out under batch conditions to study the effects of temperature, hydrogen peroxide concentration, and propylene pressure indicates that high acetol yields may be obtained at combinations of high temperatures, moderate propylene pressures, and low hydrogen peroxide concentrations.

Continuous addition conditions give better acetol yields at higher concentrations in the solvent system than do batch conditions. No doubt, better acetol yields at higher concentrations could be obtained by a more extensive study of the influence of the variables.

Interpretation of available data supports a branching sequence of oxidation reactions.

Acknowledgment

The authors thank Dr. Thomas T. Tidwell, of the Department of Chemistry, University of California at San Diego, La Jolla, Calif., for his assistance in this work.

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3

Oxidation of *p*-Methylbenzyl Radical and *p*-Xylylene

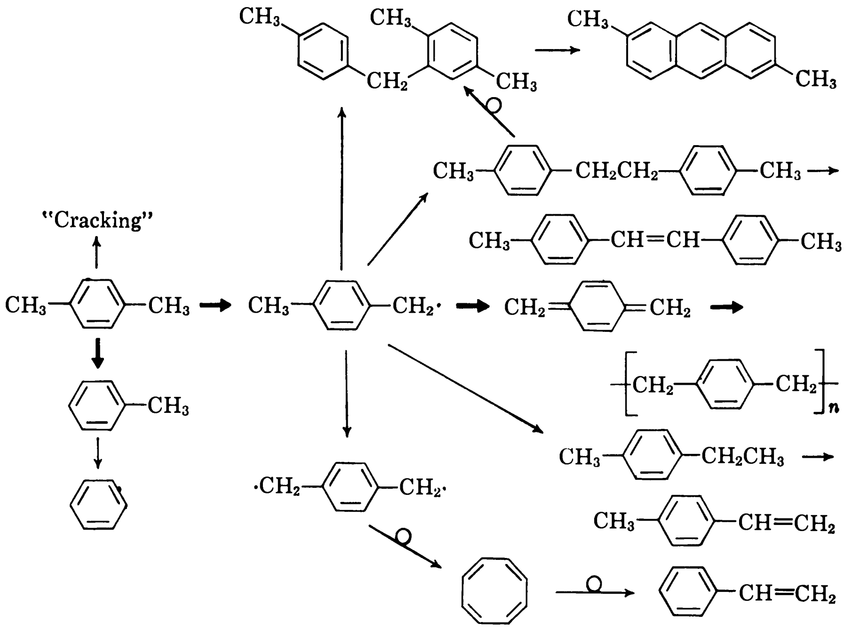
L. A. ERREDE and W. D. ENGLISH

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The fractional conversion to *p*-methylbenzyl radicals by fast flow pyrolysis of *p*-xylene at low pressure is given explicitly in terms of the pyrolysis temperature and residence time. The fractional conversion of these monoradicals to *p*-xylylene is given in terms of the pressure and the surface to volume ratio in the post pyrolysis zone. These reactive species can be oxidized to *p*-toluic acid and/or terephthalic acid by injecting oxidizing species at the appropriate point along the pyrolysis stream. The overall conversion of *p*-xylene to carboxylic acids per pass is equal to the thermal conversion of *p*-xylene to *p*-methylbenzyl radicals. This upper bound on yield per pass can be increased significantly by induced thermal decomposition of the feed stock using thermally unstable additives.

Fast flow pyrolysis of *p*-xylene at low pressure produces a mixture of products (*1*) that can be traced to a common intermediate, *p*-methylbenzyl radical (6), as outlined in the reaction scheme below. This intermediate is formed by thermal rupture of a C—H bond as the gas stream travels through the pyrolysis zone of the flow system (*12*). Most of these radicals are converted to *p*-xylylene as the pyrolyzate streams away from the furnace. Some undergo coupling to give 1,2-di-*p*-tolylethane and *p*-ethyltoluene. If these side reactions occur in the pyrolysis zone, the products continue to react to give 4,4′-dimethylstilbene and *p*-methylstyrene. In addition, ditolylethane can rearrange to *o*-methyldiphenylmethanes, which in turn are converted to the corresponding anthracenes (*1*). *p*-Xylylene that is generated in the pyrolysis zone can undergo rearrangement to cyclo-octatetraene, which in turn rearranges thermally to

styrene. Demethylation is a major competing reaction that complicates the pyrolysis.



The ratio of products formed via side reactions, indicated by light arrows, to those produced via the main reactions, indicated by the heavy arrows, increases with increasing severity of the pyrolysis conditions (*6*). A kinetic study of this pyrolysis (*6*) has shown that the fractional conversion (F) of *p*-xylene to *p*-methylbenzyl radicals is given by

$$F = k_1 t e^{-k_2 t} \tag{1}$$

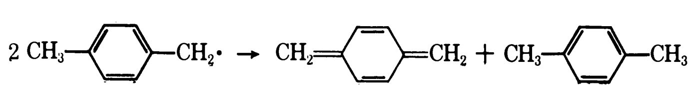
where t is the residence time in seconds, k_1 is the rate constant for formation of *p*-methylbenzyl radicals via thermal rupture of methyl C—H bond, and k_2 is the rate constant for thermal cracking of the radical intermediates. Below 1050° C., k_1 and k_2 are given by

$$k_1 = 9.3 \times 10^{13} e^{-76/RT} \tag{2}$$

$$k_2 = 2.4 \times 10^{14} e^{-78/RT} \tag{3}$$

Thus, the percent conversion as a function of residence time t and pyrolysis temperature T is a family of curves as shown in Figure 1.

Originally, it was believed that *p*-xylylene was formed via collision and disproportionation of two monoradicals within the pyrolysis zone (*12*) as indicated by:



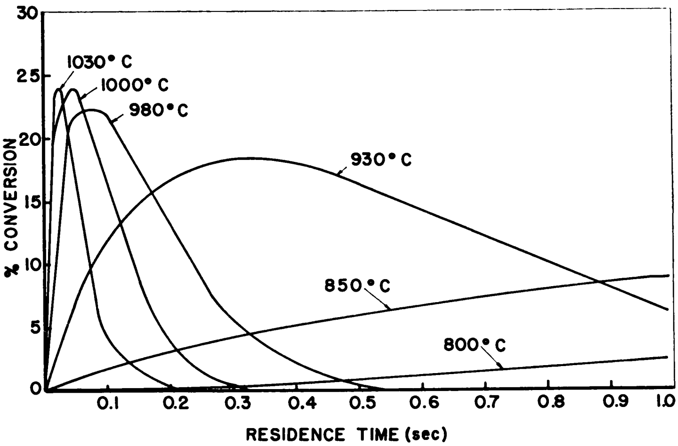


Figure 1. Percent conversion of p-methylbenzyl radicals as a function of residence time

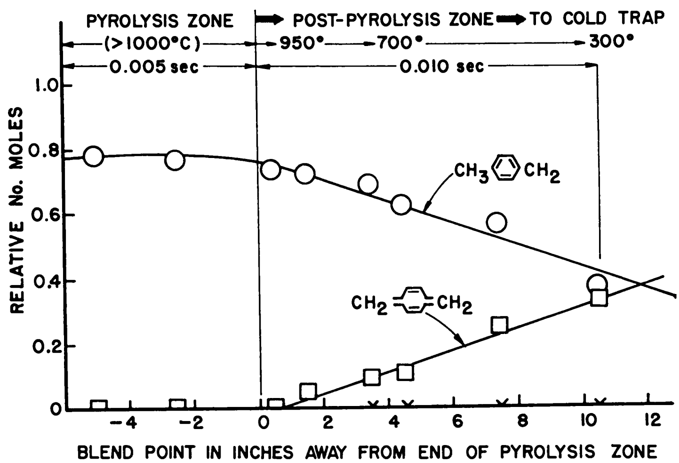
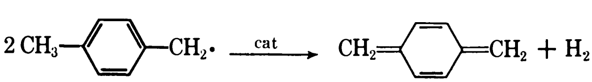


Figure 2. Relative concentration of reactive species as a function of distance away from the end of the pyrolysis zone

Subsequent studies (*3*), however, showed that *p*-xylylene is generated as the pyrolyzate streams away from the furnace, and that one molecule of *p*-xylylene is formed for every *p*-methylbenzyl radical consumed as shown in Figure 2.

The dehydrogenation occurs catalytically on the walls of the reactor, and the rate of formation is directly proportional to the surface to volume ratio in the post pyrolysis zone (*3*).



Bimolecular coupling of monoradicals to give 1,2-di-*p*-tolylethane, which is kinetically second order, competes with catalytic dehydrogenation to give *p*-xylylene, which is zero order (*3*). Thus, the square root of the ratio of coupling products (*u*) to dehydrogenation products (*W*) increase linearly with pressure (*P*) as given by:

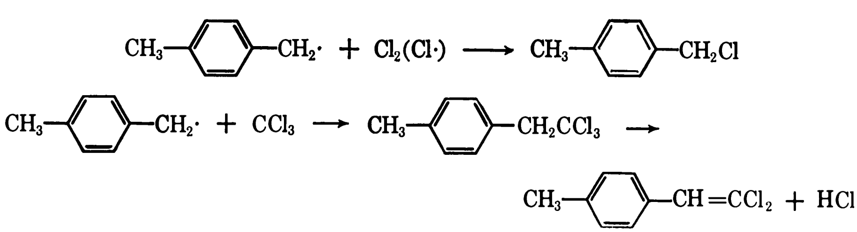
$$(u/W)^{1/2} = KP + C \tag{4}$$

where *K* and *C* are constants that depend on the ratio of surface area to volume in the post pyrolysis zone (*3*).

Accordingly, the composition of the gas stream along the pyrolysis system is predetermined by the choice of reaction conditions. The fractional conversion of *p*-xylene to *p*-methylbenzyl radicals in the pyrolysis zone is given by Equations 1–3. The subsequent conversion of these radicals to *p*-xylylene as a function of distance away from the source is given in terms of pressure and geometry by Equation 4 and Figure 2. This pyrolysis method, therefore, is a way of generating reactive species in known amount for investigating gas phase reactions.

Gas Phase Reaction with Chlorocarbon Radicals

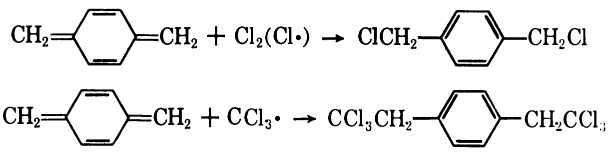
The radicals generated as described above were used as starting materials for gas phase synthesis of mono- and disubstituted derivatives of *p*-xylene. Monosubstituted derivatives were produced by quenching the *p*-xylene pyrolyzate at the exit point of the furnace with a second stream of chlorocarbon radicals generated by pyrolysis of carbon tetrachloride or hexachloroethane (*2*). In this way, mixtures of *p*-methylbenzyl chloride and β,β-dichloro-*p*-methylstyrene were produced in excellent yields based on available *p*-methylbenzyl radicals.



At these low pressures and short reaction times (< 0.01 sec.), interaction products are not produced in significant amount when the pyrolysis stream of one is quenched with the nonpyrolyzed stream of the other, proving that these products are formed via coupling of the reactive species.

Disubstituted derivatives of *p*-xylene were produced (*2*) by quenching the hydrocarbon pyrolyzate with a chlorocarbon pyrolyzate, at a considerable distance downstream from the furnace as shown in Figure 3. In this way, α,α′-dichloro-*p*-xylene and α,α′-bistrichloromethyl-*p*-xylene

were produced in good yield by quenching the hydrocarbon stream with pyrolyzed carbon tetrachloride (2) and with pyrolyzed chloroform (4, 5), respectively.



Gas Phase Reaction with Oxides of Nitrogen

When *p*-xylene and nitric acid are coaxially pyrolyzed in the apparatus shown schematically in Figure 3, and the two streams allowed to mix at a predetermined point downstream, oxidation products of *p*-xylene are obtained in good yield based on available radical species. The product composition is dependent upon the point of mixing. Thus, only

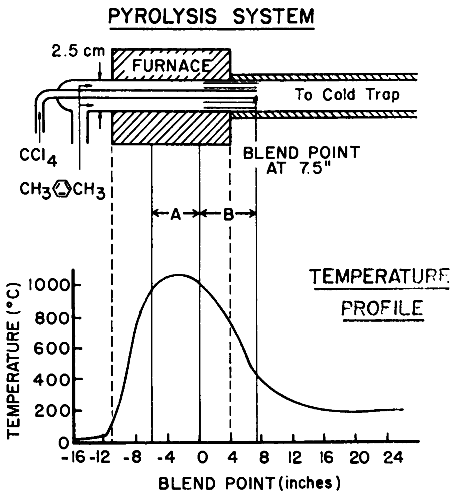
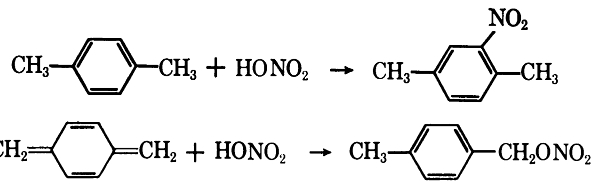


Figure 3. Diagram of pyrolysis system showing the corresponding temperature in the pyrolysis zone A and the post pyrolysis zone B

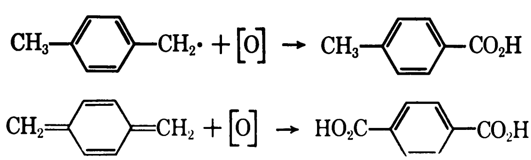
p-methylbenzoic acid was isolated when the two streams were allowed to blend within the pyrolysis zone where the hydrocarbon stream contains *p*-methylbenzyl radicals free of *p*-xylylene. On the other hand, terephthalic acid was isolated exclusively when the two pyrolyzates were allowed to blend downstream at a point where all of the *p*-methylbenzyl radicals in the hydrocarbon stream had already been converted to *p*-xylylene. A mixture of mono- and dicarboxylic acid was obtained when the hydrocarbon stream was quenched at an intermediate point. Aromatic

aldehydes were obtained as the major product when the reaction was carried out using a limited amount of pyrolyzed nitric acid. In these experiments the conversion of *p*-xylene to oxidation products was equal to the expected conversion to *p*-methylbenzyl radicals indicating a one to one correspondence of radicals generated with oxidation products formed.

When a low pressure stream of pyrolyzed *p*-xylene was quenched at 400° C. with nonpyrolyzed nitric acid and the resultant gas mixture collected in heptane kept at —78° C., the major products isolated were not carboxylic acids, but rather a mixture of mono- and dinitroxylenes and *p*-methylbenzyl nitrate (7). Similar results were obtained when the hydrocarbon pyrolyzate was collected in a mixture of nitric acid and heptane kept at —78° C. The total yield of products was considerably higher than the amount of reactive species generated thermally. It was concluded, therefore, that the nitroxylenes were formed by direct nitration of *p*-xylene in gas phase and in solution. The *p*-methylbenzyl nitrate was formed by adding nitric acid to *p*-xylylene in solutions (9).



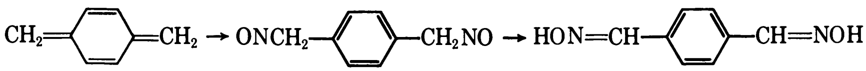
Only trace amounts of carboxylic acids were isolated, indicating that little if any gas phase oxidation of the radicals had occurred. Similarly, no carboxylic acids were isolated when a low pressure stream of pyrolyzed nitric acid was quenched with nonpyrolyzed *p*-xylene; only a relatively small amount of nitration products were isolated presumably via reaction with unchanged nitric acid. These results demonstrate that the oxidation products are produced by gas phase reaction of the hydrocarbon radicals with the thermal degradation products of nitric acid and not with nitric acid itself since the latter gives only nitration products.



Nitric acid is known to decompose thermally to produce reactive fragments such as HO·, nitrogen dioxide, and atomic oxygen. Indeed, large quantities of nitrogen dioxide were isolated in the cold traps when excess amounts of nitric acid were pyrolyzed in these experiments. This observation suggested that nitrogen dioxide per se might effect gas phase thermal oxidation of hydrocarbon radicals. Accordingly, a low pressure stream of pyrolyzed *p*-xylene was mixed with nitrogen dioxide at about

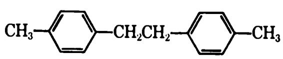
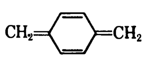
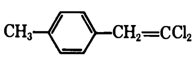
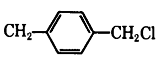
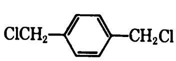
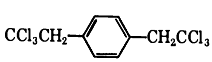
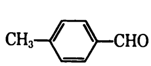
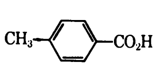
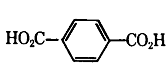
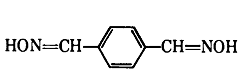
200° C. where most of the monoradicals had already been converted to *p*-xylylene. A mixture of low molecular weight acidic products with nitrogen-containing substituents on terminal methylene carbon atoms was isolated, indicating that the temperature at which coupling occurred was not high enough to cause thermal degradation of nitrogen-containing end groups. When the two streams were allowed to blend at 600° C., however, a mixture of *p*-toluic acid and terephthalic acids was obtained in the ratio of about 2:1, which corresponds to the ratio of *p*-methylbenzyl radicals to *p*-xylylene at the point of mixing.

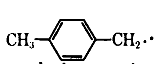
Terephthaldoxime is obtained when the *p*-xylene pyrolyzate is quenched below 200° C. with nitric oxide. A more complicated product mixture



is obtained when the two streams are mixed at high temperature owing to thermal degradation of the nitroso product. Some of the products iso-

Table I. Compounds Prepared via Gas Phase Reaction

		Experimental
Compound Isolated	*Yield*[a]	*Catalyst*
	100	none
	80	surface char
	40	none
	40	none
	80	surface char
	10	surface char
	50	none
	80	none
	90	char
	80	char

[a] Yield based on available  as calculated using Equation 1.

[b] Distance away from the pyrolysis zone in inches.

lated via gas phase synthesis and their respective yields are shown in Table I.

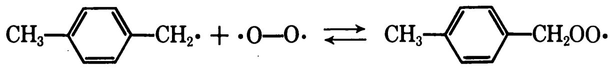
Reactions with Molecular Oxygen

Since molecular oxygen is used to convert gaseous *p*-xylene at atmospheric pressure to toluic acid, it was speculated that this method might be used to generate *p*-methylbenzyl radicals at low pressure. It was shown, however, that although atomic oxygen is a good oxidizing agent for these radicals in low pressure gas streams, molecular oxygen is not. Thus, only a trace amount of toluic or terephthalic acid was obtained when *p*-xylene and oxygen were subjected to fast-flow copyrolysis at low pressure (less than 10 mm.). Even when the oxygen to *p*-xylene ratio was 3:1, the major products isolated were those normally produced via fast flow pyrolysis of *p*-xylene. Moreover, the oxygen present did not interfere with the catalytic conversion of *p*-methylbenzyl radicals to *p*-xylylene. In another experiment performed by Szwarc (*13*) oxygen was recovered

with p-Methylbenzyl Radicals

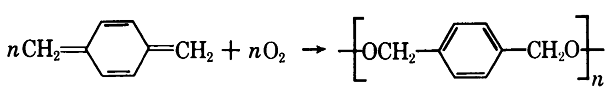
Conditions in Post Pyrolysis Zone		
Quench Point[b]	*Second Radical Stream*	*Reference*
none	none	3
none	none	3
0	pyrolyzed CCl_4	2
0	pyrolyzed CCl_4	
8	pyrolyzed CCl_4	2
5	pyrolyzed $CHCl_3$	5
0	pyrolyzed HNO_3 in limited amount	
0	excess HNO_3	
8	excess HNO_3	
16	excess NO	

quantitatively when a low pressure oxygen–*p*-xylene gas mixture was subjected to fast flow pyrolysis at 1000° C. These observations are in sharp contrast to the ease with which oxidative interaction occurs at atmospheric pressure. Apparently the formation of benzyl peroxy radicals is a reversible reaction, and the equilibrium is far to the left at very low pressure.

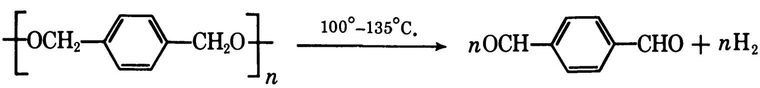


That the formation of alkylperoxy radicals can be a reversible reaction was also observed by Matsugashita and Shinohara (*11*). These workers reported that addition of oxygen to polymeric perfluorocarbon radicals gives the corresponding polymeric perfluorocarbon peroxy radicals. The original radical species are obtained when the partial pressure of oxygen in contact with the polymer is markedly decreased.

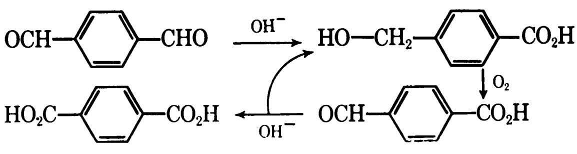
Interaction of molecular oxygen with *p*-xylylene occurs readily, however, if the *p*-xylylene is collected in a solvent kept at —78° C. and the resulting solution aerated with oxygen (*8*). This procedure causes quantitative conversion of the diradical-like hydrocarbon molecule to poly-(*p*-xylylene)peroxide within 15 minutes.



When dispersed in water, the polymeric peroxide can be decomposed thermally to give terephthaldehyde and hydrogen in good yield.



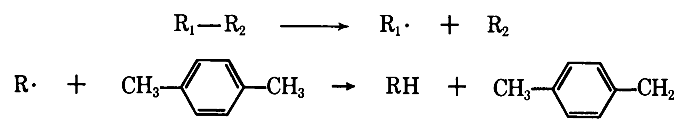
If the decomposition is carried out in aerated alkaline water, terephthalic acid is the product isolated owing to the ease with which the dialdehyde undergoes the Cannizzaro reaction and ease with which the alcohol carboxylic acid undergoes reoxidation to the aldehyde acid.



Alternatively, *p*-xylylene glycol can be obtained exclusively by decomposing the polymeric peroxide dispersed in an aqueous solution of a reducing agent.

Induced Thermal Decomposition of p-Xylene

As described previously, the overall yield per pass of reaction product corresponds to the available radicals generated thermally; hence, the limitation on overall yield per pass is dependent upon thermal conversion of the feed stock to *p*-methylbenzyl radicals as shown in Figure 1. The best conversion of *p*-xylene to *p*-methylbenzyl radicals per pass, however, approaches only 35% (*6*). Moreover, the selectivity of this level is less than 70% and decreases further with increasing severity of the pyrolysis conditions. The earlier work of Szwarc (*13*) suggested that this upper limit on yield and conversion might be increased by adding thermally unstable compounds, such as *tert*-butyl peroxide, to the pyrolysis feed stock. The radical fragments produced by thermal degradation of the additive would in turn generate *p*-methylbenzyl radicals by hydrogen abstraction from *p*-xylene.



Similar results were obtained by Schaefgen (*10*), who demonstrated that conversion of *p*-xylene at 727° C. and 0.016 sec. residence time to *p*-methylbenzyl radicals could be increased from a negligibly small amount to about 22% by adding ethylene oxide to the feed stock. The ethylene oxide was decomposed completely at these pyrolysis conditions to afford large quantities of methyl radicals that attacked *p*-xylene giving *p*-methylbenzyl radicals. Little or no *p*-xylylene was isolated, however, since coupling with excess CH_3· converted the benzyl radicals to *p*-methylethylbenzene or its subsequent dehydrogenation product *p*-methylstyrene. This experiment was repeated in our laboratory using limited amounts of ethylene oxide, and again conversion to *p*-methylbenzyl radicals was improved over that anticipated for *p*-xylene alone as summarized in Table II. *p*-Xylylene was isolated in the usual way, and the efficiency for conversion from *p*-methylbenzyl radicals was a function of pressure as described previously.

Table II. Induced Decomposition of p-Xylene Using Ethylene Oxide

Ratio of p-Xylene to Ethylene Oxide	*Pyrolysis Conditions*			*Product*		
	T° C.	*[a]t, sec.*	*Pmm*	*Calc. Conv. for p-Xylene[b]*	*Obs. Conv.*	*[a]u/W*
∞	960	0.022	25	6.5	4.2	2.5
∞	956	0.008	10	3.0	2.7	0.6
6.0	896	0.024	10	2.0	8.6	0.8
2.3	900	0.033	10	2.5	10.	0.8
2.1	910	0.034	20	4.0	11.	2.5

[a] Symbols: *t*—residence time, *u*—*p*-methylbenzyl radicals isolated as 1,2-di-*p*-tolyethane, *W*—*p*-xylylene isolated as poly-*p*-xylylene.
[b] Value calculated using Equations 1–3.

Mixtures of *p*-xylene and *p*-methylbenzyl halides were copyrolyzed, and the yield of reactive species isolated as terephthalic acid again was improved over that expected for *p*-xylene alone as shown in Table III. All of the *p*-methylbenzyl radicals generated in the pyrolysis zone were dehydrogenated in the post pyrolysis zone where the pressure was (<4 mm.) and the ratio of surface to volume was large. The *p*-xylene was then oxidized to terephthalic acid by blending with pyrolyzed nitric acid.

Table III. Induced Thermal Decomposition of p-Xylene Using p-Methylbenzyl Halide

Halide	Ratio of p-Xylene to Halide	Pyrolysis Conditions T° C.	Pyrolysis Conditions t, sec.	Calc. Conv. for p-Xylene	Obs. Conv. for p-Xylene
Chloride	14	1050	0.005	11	20
	14	980	0.005	5	19
	10	800	0.005	0.5	3
Bromide	14	1100	0.01	27	44
	14	1000	0.05	25	43
	14	900	0.05	3	15
	14	840	0.1	1	9
	9	840	0.1	1	8
	4	800	1.0	1	21

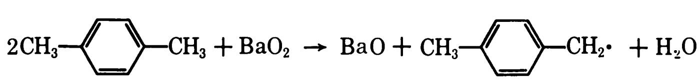
As described earlier, significant oxidation did not occur when *p*-xylene and oxygen were copyrolyzed at low pressure. Moreover, the conversion of *p*-xylene to *p*-methylbenzyl radicals was about the same as that expected for pyrolysis of *p*-xylene per se. An increase was manifested, however, when copyrolysis of *p*-xylene and oxygen was carried out at <4 mm. in the presence of barium oxide as shown in Table IV.

Table IV. Induced Thermal Decomposition of p-Xylene using Oxygen

Pyrolysis conditions T° C.	Pyrolysis conditions t, sec.	Pyrolysis conditions Cat. Surface	Experiment Sequence	Calc. Conv. for p-Xylene	Obs. Conv. with Oxygen
990	0.005	none	1	6	7
960	0.005	none	3	3	6
960	0.004	BaO	2	3	10
950	0.004	BaO	4	2	9

The significant increase in conversion using barium oxide surface suggests a surface redox system perhaps as outlined below:

$$2BaO + O_2 \rightarrow BaO_2$$



Experimental

Copyrolysis of *p*-Xylene and Nitric Acid. The pyrolysis system shown in Figure 4 was modified to include a second vaporizer for metering aqueous nitric acid (68%). The system was evacuated to 6 mm., and

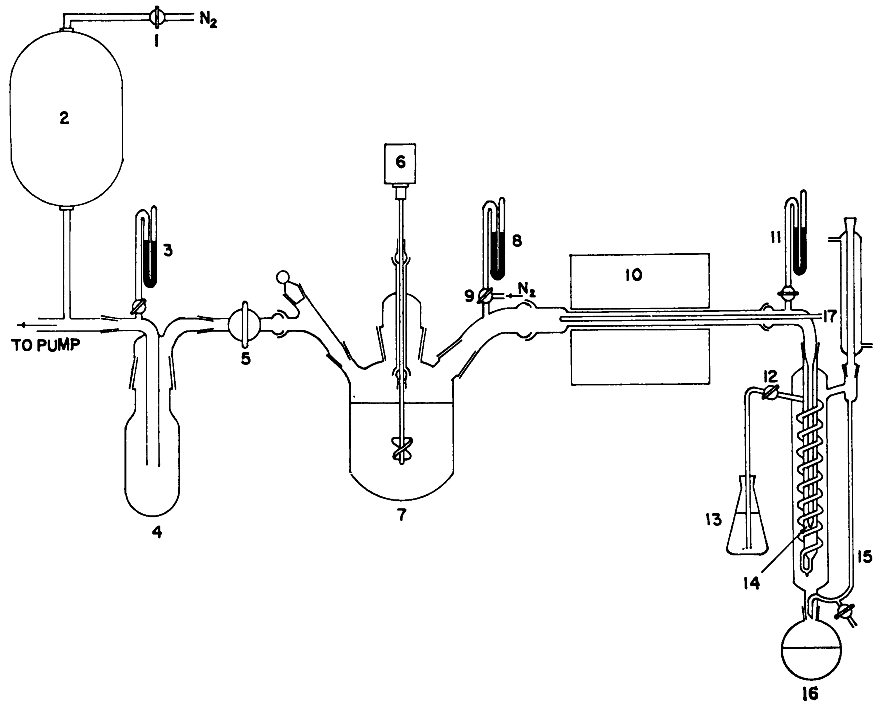


Figure 4. Pyrolysis apparatus

p-xylene (3.17 moles) and nitric acid (1.05 moles) were metered to the system at the rate of 0.045 and 0.015 moles/min., respectively. The two gas streams were mixed before they entered the furnace where fast flow pyrolysis occurred at 1030° C. The pyrolysate was collected in 4 liters of hexane kept at —78° C. The cold trap was warmed to room temperature to afford a three-phase mixture of hexane solution, aqueous acid solution (43 grams), and a black tar (9 grams). Large volumes of nitrogen dioxide were given off when the mixture was warmed to room temperature. The last traces were removed by a current of nitrogen. The hexane solution was washed with water, and the solvent was removed by rapid evaporation at 100° C. and 60 mm. The yellow, liquid residue (154 grams) was a mixture of aldehydes and aromatic hydrocarbons having no NO_2 groups as indicated by infrared analysis and negative qualitative test for NO_2 using ferrous ammonium sulfate in alcoholic potassium hydroxide. The mixture was separated by distillation at atmospheric pressure to give three main fractions. Fraction 1 (76 grams, b.p. 137°–141° C.) was identified by infrared analysis as *p*-xylene. Fraction 2 (32 grams, b.p. 196°–202° C., $n^{14}D$ 1.5433) was identified as *p*-tolualdehyde (lit. b.p. 204°–205° C., $n^{14}D$ 1.5483) by infrared analysis and by converting a sample to its 2,4-dinitrophenylhydrazone derivative (m.p. 229°–230° C., no depression with authentic sample) in good yield. Fraction 3 (35 grams of residue) was separated further by distillation at 2 mm. to give three additional major fractions. (a) Infrared analysis indicated

that this (2.2 grams, b.p. 64°–80° C.) was mostly *p*-tolualdehyde with some 1,2-di-*p*-tolylethane and diarylmethanes present as impurities. (b) Infrared analysis indicated that this (18.7 grams, b.p. 125°–137° C.) was a mixture of 1,2-di-*p*-tolylethane, diarylmethanes, and a small amount of acid material. The mixture was extracted with dilute sodium hydroxide, and the residue was dissolved in methanol. The methanol solution was chilled to −78° C. to precipitate 1,2-di-*p*-tolylethane (4.5 grams) in the form of pearl-white platelets (m.p. 74°–75° C., no depression with authentic sample). The methanol solution was evaporated to dryness leaving a residue (10 grams) which was a mixture of alkylated diphenylmethanes and 1,2-di-*p*-tolylethane as indicated by infrared analysis. (c) Infrared analysis indicated that this (9 grams residue, b.p. >150° C.) was a complex mixture of aromatic hydrocarbons and some acidic material. The residue was leached with dilute sodium hydroxide. The alkaline extract was combined with corresponding extract from fraction b, and the resulting solution was acidified with hydrochloric acid to liberate the organic acid (3 grams) which was removed by filtration. The acid was recrystallized from hot water to yield *p*-toluic acid in the form of fine, white needles (m.p. 174°–175° C., no depression with authentic sample). The compound was also identified by infrared spectrum.

Thus, 3.2 moles of *p*-xylene and 1.05 moles of nitric acid were copyrolyzed to afford 0.28 mole of *p*-tolualdehyde, 0.02 mole of *p*-toluic acid, and 0.24 mole of *p*-methylbenzyl radical equivalents isolated as the products 1,2-di-*p*-tolylethane and diarylmethane (*1*).

Coaxial Pyrolysis of *p*-Xylylene and Nitric Acid. The internal Thermowell No. 17 of the pyrolysis system shown in Figure 4 was replaced by an open-end quartz tube through which nitric acid could be metered to the pyrolysis system. This tube extended to a point 3 inches beyond the furnace so that blending of the pyrolyzed nitric acid stream and the pyrolyzed *p*-xylene stream would occur at a point 6.5 inches away from the pyrolysis zone (Figure 3). The space in the outer concentric tube between the pyrolysis zone and the blend point was filled with five quartz tubes (6 inches long, 6 mm.–o.d., 4 mm.–i.d.) to ensure complete conversion of *p*-methylbenzyl radicals to *p*-xylylene in the *p*-xylene pyrolysate before the hydrocarbon stream reached the blend point (*3*). The temperature was recorded by means of a sliding thermocouple placed between the furnace and the outer pyrolysis tube. The system was evacuated to 4 mm., and *p*-xylene (1.98 moles) and nitric acid (3.4 moles) were metered separately to the system through the concentric tubes at the rate of 0.016 and 0.027 moles/mm., respectively. Pyrolysis of *p*-xylene occurred at 930° C. for 0.01 sec. (conditions which are known to give about 0.24 mole of *p*-methylbenzyl radicals (*6*)). The pyrolysate mixture was collected in hexane (4 liters) kept at −78° C. The resulting mixture was warmed to room temperature with evolution of much nitrogen dioxide. The last traces were removed by a stream of nitrogen. A three-phase system was obtained, and this was separated into its aqueous acid, organic liquid, and organic solid components. The solid (27 grams) was dissolved in aqueous sodium carbonate. The organic phase was extracted with aqueous sodium carbonate. The two alkali carbonate solutions were combined and then acidified with aqueous hydrochloric acid. The organic acid liberated (26 grams, 0.16 mole) was collected by filtration. The acid was leached with methanol, but none dissolved, indicating the

absence of *p*-toluic acid. The acid did not melt below 300° C. Its infrared spectrum was virtually identical with that of terephthalic acid. A small sample was converted to its dimethyl ester by treatment with fused phosphorus pentachloride and subsequent addition to methanol. The melting point of the dimethyl terephthalate (m.p. 138°–139° C.) produced in this way showed no depression when mixed with an authentic sample. The hexane solution was evaporated to dryness and a mixture of the usual aromatic hydrocarbons (*1*) was obtained as residue (9 grams).

Thus, pyrolysis of *p*-xylene (1.98 moles) was carried out in such a way as to afford about 0.24 mole of *p*-methylbenzyl radicals. About 70% of these were isolated as terephthalic acid and about 30% as a mixture of aromatic hydrocarbons (1,2-di-*p*-tolylethane, methylated diphenylmethanes, and anthracenes).

Coaxial Pyrolysis of *p*-Xylene and Nitrogen Dioxide. The internal Thermowell No. 17 of the pyrolysis system shown in Figure 4 was replaced by an open-end tube through which nitrogen dioxide was led into the system, which was evacuated to 5 mm. *p*-Xylene (7.3 moles through the outer tube) and nitrogen dioxide (25.6 moles through the inner tube) were metered to the system at the rate of 0.0545 and 0.175 mole/min., respectively. Pyrolysis of *p*-xylene occurred at 1000° C. for 0.002 sec., and the two pyrolyzate streams were allowed to blend at a point 6.5 inches away from the end of the mutual pyrolysis zone. Previous experiments had shown that the pyrolysis conditions used in this experiment afford about 0.18 mole of *p*-methylbenzyl radicals (*6*), and that about 40% of these are converted to *p*-xylylene by the time the hydrocarbon stream reaches the blend point (Figure 3) where the temperature is about 450° C. The pyrolysate mixture was collected in hexane kept at −78° C. When the resulting solution was warmed to room temperature, the usual three-phase mixture was obtained. The solid (9 grams) was removed by filtration, dissolved in aqueous sodium carbonate, and reprecipitated by addition of hydrochloric acid. This product was identified as terephthalic acid by its infrared spectrum. The organic layer was extracted with aqueous sodium carbonate. Acidification of the extract with dilute hydrochloric acid gave 11 grams of impure *p*-toluic acid (165°–170° C.). The organic layer was evaporated to dryness, and a mixture of aromatic hydrocarbons (1,2-di-*p*-tolylethane and diarylmethanes) was obtained as residue (6 grams).

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4

Catalytic Oxidation of Isobutylene to Methacrolein over Copper Oxide Catalysts

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The air oxidation of isobutylene was investigated over supported and unsupported copper oxide catalysts in an isothermal integral flow reactor. The effect of several variables—ratio of oxygen to isobutylene in the feed, process temperatures, copper concentrations of the catalysts, and reciprocal of space velocity on the conversion and yield—were determined. Though several mechanisms were postulated, the rate of reaction was most satisfactorily correlated by a mechanism which assumes the rate-controlling step as the surface reaction between strongly adsorbed isobutylene and gaseous (weakly adsorbed) oxygen. The rate ex-

$$r = \frac{\alpha K_{C_4H_8} P_{C_4H_8} P_{O_2}}{1 + K_{C_4H_8}P_{C_4H_8} + K_{C_4H_8O}P_{C_4H_6O}}$$

pression fitted the data very well.

Owing to the likely occurrence of complete oxidation to carbon dioxide and water, comparatively few studies have been carried out on the vapor phase catalytic oxidation of olefins on metal oxides. The selective oxidation of ethylene to ethylene oxide (*7*), propylene to acrolein (*18*), and various aromatics to aromatic dicarboxylic acids or anhydrides represent cases of considerable industrial importance. Though several patents (*1, 3, 4, 5, 6, 8, 9, 14*) have appeared during the past few years describing the use of various metal oxides in the partial oxidation of isobutylene to methacrolein, scientific literature describing the effects of various operating variables on the composition of products is quite limited. The gas phase oxidation of isobutylene has been examined by a static method between

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252° and 320° C. by Skirrow and Williams (*17*). They obtained carbon dioxide, carbon monoxide, water, propylene, acetone, formaldehyde, acetaldehyde, isobutylaldehyde, methacrolein, propylene oxide, methane, and acetic acid as reaction products. The formation of the more important products has been accounted for in terms of a radical addition mechanism, initiated by addition of a hydroxyl radical to the terminal CH_2 group and followed by peroxy radical formation and its subsequent decomposition. Bretton, Wan, and Dodge (*2*) studied the effects of experimental variables, contact time, bed temperature, and air/hydrocarbon ratios on the conversion and yields of product for the oxidation of hydrocarbons containing four carbon atoms on V_2O_5 supported on Alfrax. In the case of isobutylene oxidation, they obtained acetic acid, methacrolein, and formaldehyde besides carbon dioxide, carbon monoxide, and water. The formation of the reaction products has been explained by a scheme of atomic dehydrogenation and peroxidation similar to that suggested by Waters (*20*), and by peroxide decomposition. Popova, Milman, and Latysheva (*15*) studied the oxidation of isobutylene to methacrolein at 350°–70° C. in the presence of a 0.1–1.5% copper oxide (70% Cu_2O + 30% CuO) catalyst supported on a Silite base, using an isobutylene/oxygen ratio of 5.6:1. On oxidation, 3.8% of the isobutylene was converted to carboxyl compounds, 82.5% of which was methacrolein, the balance being propionaldehyde, acetaldehyde, and acrolein.

The air oxidation of isobutylene was investigated over several supported and unsupported copper oxide catalysts alone or mixed with other metal oxides in an isothermal integral flow reactor. The effect of several variables—ratio of oxygen to isobutylene in the feed, process temperature, copper concentration, reciprocal of space velocity—on the conversion and yield was determined. Based on experimental data, the rate-controlling step and the rate equation for the partial air oxidation of isobutylene were determined.

Experimental

The experimental apparatus used to study the reaction is shown schematically in Figure 1. The reactants, dry air, and chemically pure isobutylene (min. 99% purity) were obtained from high pressure, diaphragm type regulators, whereby the pressure of air and isobutylene were reduced to 20 p.s.i.g. and metered over Brooks rotameters. The gases were mixed and preheated before entering the reactor. The preheating section, consisting of a 3 foot long $^1/_8$ inch—o.d., 316 stainless steel tubing wound around the reactor, was immersed in a constant temperature metal bath. The reactor was heated in a liquid metal (50% bismuth, 50% lead) bath, which in turn was situated in an electrically heated furnace, whose temperature was controlled to within ±3° C. by a Honeywell Pyrovane temperature controller. The catalyst bed consisted of copper oxide sup-

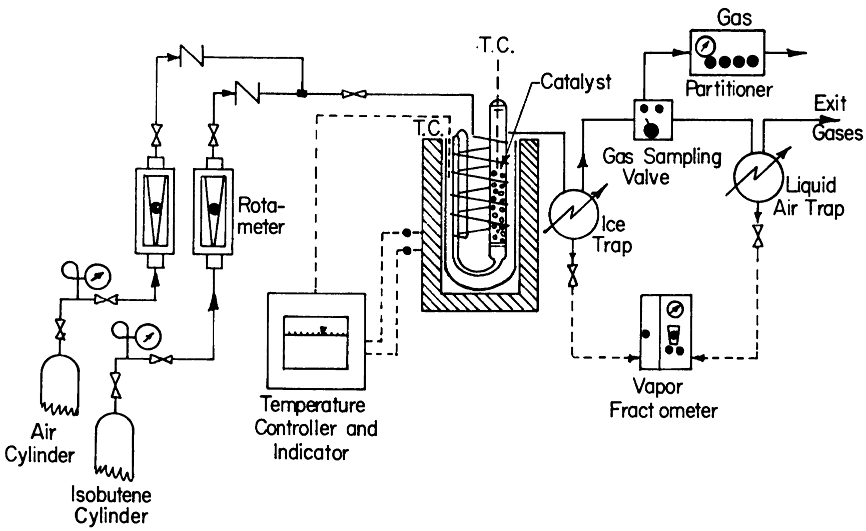


Figure 1. Flow diagram for the air oxidation of isobutylene

ported alone or mixed with another oxide, placed in a 0.5 inch—i.d. 304 stainless steel reactor, held in place by a stainless steel porous plate in the bottom and steel wool at the top.

Thermocouples placed at the center of the catalyst bed in the reactor, and in the metal bath surrounding it, recorded the same temperatures at high flow rate of gases, indicating that the preheating section was long enough to heat the entering gases up to the desired temperature. However, during the course of catalytic reaction, these thermocouples recorded a difference of about 7° C., which could be considered as negligible. The reaction has therefore been treated as virtually taking place under isothermal conditions, considering the highly exothermic nature of the reaction.

Procedure. For the start of the run, air was slowly passed through the reactor, while the catalyst was brought to the required temperature. When the required temperature was attained, isobutylene and air ratios were adjusted to the desired values and maintained at the specified rates over a period of 15 minutes, and the reactor was brought to steady state. The steady state run was continued for 30–60 minutes by collecting the liquid sample from the exit gases in an ice cooled trap (Trap I). The noncondensed gases were passed through a sampling valve leading to a Fisher Gas Partitioner. The off gases from the sampling valve were passed through a liquid air trap (Trap II). Part of the aldehydes which did not condense in Trap I condensed in Trap II.

Analytical. The total acid content was obtained by titrating the condensate from ice-cooled trap with 0.055*N* KOH solution. Very little acid was present in the condensate and was considered too insignificant to affect the material balance; as such, it was not included in the analysis of the products. The condensate from Trap I contained minor quantities of aldehydes.

GASES. The inlet feed gas and exit product gases were analyzed for isobutylene, carbon monoxide, carbon dioxide, oxygen, and nitrogen by periodic injection of 0.5 ml. sample into Gas Partitioner containing a 6-foot hexamethyl phosphoramide column and a 13-foot 13 X molecular sieve column connected in series. Nitrogen was obtained by difference.

ALDEHYDES. The sample from the liquid air trap was diluted with approximately 8 ml. of diethyl ether and placed in a refrigerator which was kept at 5° C. Once temperature equilibrium was reached, .005 ml. of the mixture was injected into a 154D Perkin-Elmer gas chromatograph, containing two 4-meter columns of Carbowax 1500 on Teflon. The column could separate acetone, acetaldehyde, propionaldehyde, crotanaldehyde, acrolein, methacrolein, and water. Only methacrolein, water, and traces of acetone and acetaldehyde were obtained with all catalysts except catalyst VIII and catalyst IX.

Catalysts. Catalyst I, a pumice-supported copper oxide catalyst (16 wt.% of copper) was prepared by impregnating 20–40 mesh crushed pumice stone with copper nitrate solution. Catalyst II (2% copper), Catalyst III (8% copper), and Catalyst IV (32% copper) were prepared by impregnating pumice with the required amount of copper nitrate solutions. Catalyst V, an unsupported copper oxide catalyst, was prepared by calcining copper nitrate for two hours at 200° C. and four hours at 550° C. Catalyst VI, a molybdenum oxide catalyst supported on pumice (8% MoO_3) was prepared by impregnating pumice with an ammonium paramolybdate solution. Catalyst VII, a copper-molybdenum oxide catalyst (75% CuO + 25% MoO_3) was prepared by impregnating the pumice with a copper nitrate plus ammonium paramolybdate solution, containing copper oxide and molybdic oxide in required ratios. Catalyst VIII, a copper oxide supported on alumina (16% copper) was prepared by impregnating alumina with copper nitrate solution. Catalyst IX, a mixed oxide catalyst (8% oxides, MoO_3, V_2O_5, P_2O_5 in a ratio of 5:1:0.6) was prepared by impregnating alumina with an ammonium paramolybdate-ammonium vanadate-ammonium phosphate solution containing required ratios of oxides. All the catalysts except Catalyst V were dried overnight at 105° C. and calcined at 550° C. for six hours. Each catalyst was activated by placing it in the flow reactor and passing a slow stream of air over it for 12 hours at 400° C.

Results and Discussion

The effect of oxygen (in the air)/isobutylene in the feed, the operating temperature, and the copper concentration in the catalyst on the conversion of isobutylene and the yield of methacrolein were investigated. While conversion is referred to as the moles of isobutylene consumed (reacted) per hour to the moles of isobutylene fed per hour, the ratio of the moles of methacrolein produced per hour to the moles of isobutylene reacted per hour has been defined as yield of methacrolein. For carbon dioxide and carbon monoxide, the yield has been defined as one-fourth of the ratio of the moles of carbon monoxide or carbon dioxide formed to the moles of isobutylene reacted. The ratio of grams of catalyst to the

Table I. Conversions and Yields for Different Catalysts

$T = 400°$ C., $N = 1$, $W/F = 1.71$

Catalyst	Conversion of Isobutylene	Yields C_4H_6O	CO	CO_2	Acids	Other Aldehydes
I	0.400	0.296	0.688	0.009	—	—
II	0.272	0.333	0.651	0.013	—	—
III	0.371	0.308	0.678	0.012	—	—
IV	0.422	0.274	0.717	0.009	—	—
V	0.467	0.069	0.840	0.098	—	—
VI	negligible					
VII	0.386	0.301	0.682	0.009	—	—
VIII	0.526	0.181	0.532	0.171	0.010	0.106
IX	0.618	0.273	0.383	0.083	0.046	0.215

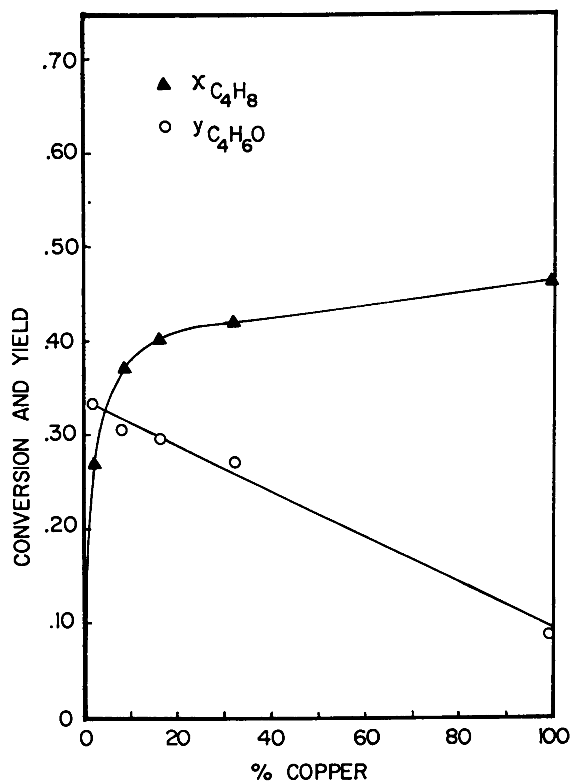


Figure 2. Effect of copper concentration on the conversion and yield

gram mole of isobutylene fed per hour is defined as W/F. The ratio of W/F was varied by varying the amount of catalyst while keeping the amount of feed constant, and vice-versa.

Effect of Various Catalysts on Oxidation. The effect on the conversion and yield for several catalysts at 400° C., a W/F ratio of 1.71, and an

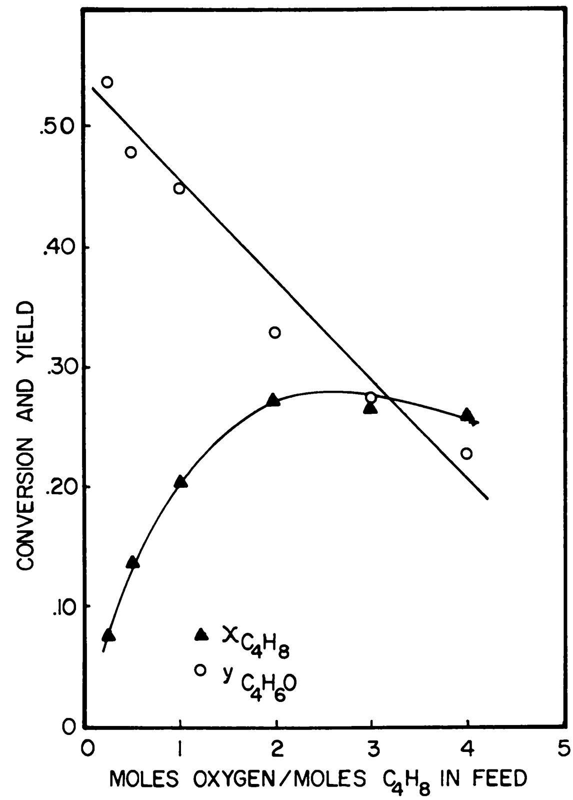


Figure 3. Effect of oxygen/isobutylene ratio in feed (N) on conversion and yield

oxygen/isobutylene ratio of 1.0 is given in Table I. Though catalyst IX gave the highest conversion, catalyst I was considered the best for the detailed kinetic study. It had negligible activity towards the formation of organic compounds other than methacrolein and a very high selectivity for methacrolein production at a high rate of conversion. This catalyst was used therefore throughout the investigation of the reaction kinetics.

Effect of Copper Concentration. The oxidation of isobutylene was carried out over several copper oxide catalysts containing varying amounts of copper oxide/support ratios. Figure 2 shows the effect of copper concentration in the catalyst on the conversion of isobutylene at 400° C., a W/F ratio of 1.71 and an $N = 3.0$. It increased fairly rapidly up to a concentration of 10% copper by weight. For higher concentrations, the effect on the conversion was much less pronounced, though it increased steadily up to a value of 0.467 for unsupported copper oxide. An increase in copper content of the catalyst, on the other hand, adversely affected the yield of methacrolein. The decrease in the yield of methacrolein seems to be directly proportional to an increase in copper content of the catalyst.

Effect of Oxygen/Isobutylene Ratio. The effect of oxygen/isobutylene ratio (N) in the feed on the conversion and yield for a W/F ratio of 1.0 over copper oxide supported on pumice (Catalyst I) at 400° C. is shown in Figure 3. The conversion of isobutylene increased rapidly with reactant ratios up to an N of 2 and then seemed to become independent of the reactant ratios.

Effect of Temperature. The influence of the temperature and yield over Catalyst I was investigated in the temperature range 350°–450° C.

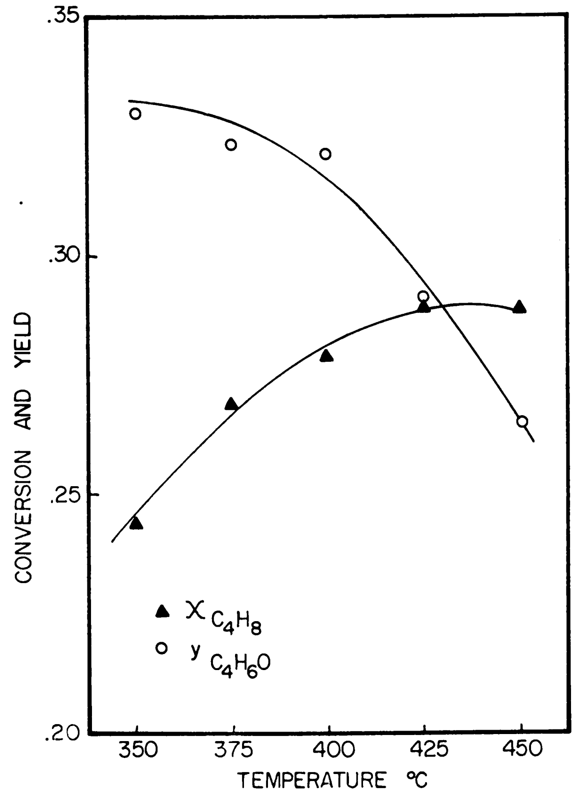


Figure 4. Effect of temperature on conversion and yield

Figure 4 shows the effect of temperature on the conversion and yield at a W/F ratio of 1.2 and $N = 2.0$. With increasing temperature from 350° to 450° C., the conversion increased but the yield decreased.

Effect of W/F Ratios. Figure 5 shows the effect of various W/F ratios on the conversion of isobutylene and the yield of methacrolein and carbon dioxide at 400° C. and an N of 1.0 over Catalyst I. It is seen that though the fraction of isobutylene consumed (% conversion) increased

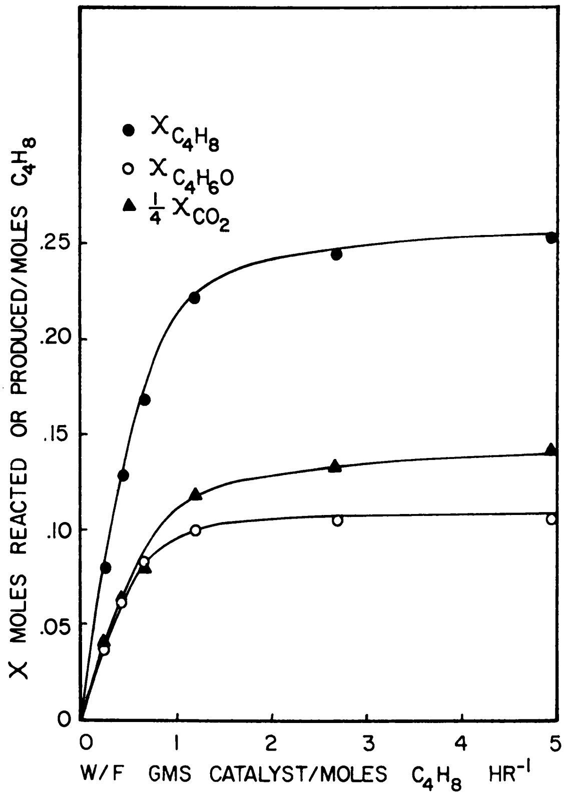


Figure 5. Effect of W/F ratios on conversions and yields

rapidly up to a W/F ratio of 2, there is not much change in the conversion of isobutylene for W/F exceeding 2.

Figures 2, 3, and 4, show that while the methacrolein yield decreases with increased copper concentrations, temperature or oxygen/isobutylene ratio in the feed, the yield of carbon dioxide, carbon monoxide, and water increased. These results suggest that methacrolein underwent further oxidation to carbon dioxide and monoxide. The above results are in line with the findings of Isaev, Margolis, and Sazanova (*12*) and Voge, Wagner, and Stevenson (*19*), who oxidized propylene over cuprous oxide catalysts. They established, by means of kinetic and isotopic data, that most of the carbon dioxide formed in the process results from the oxidation of acrolein.

A kinetic analysis of the experimental data (*16*) was made using the Hougen-Watson (*11*) approach, whereby various mechanisms which might control the reaction rate are postulated, and the rate expressions consistent with these hypotheses are derived. The rate-controlling mecha-

nism of the solid-catalyzed gas reaction may be the mass transfer of the reactants or products or chemical reaction of adsorbed molecules at the catalyst surface. The rate expressions thus derived are then fitted to the experimental data. The rate expression which gives the best fit is retained; the others are discarded.

The effects of diffusion and mass transfer were kept at a minimum by using a high velocity of gas through the catalyst bed. The use of inert porous support and its small particle size (20–40 mesh) and surface area (less than 0.1 sq. meter/gram) ruled out the possibility of the diffusion in the pores controlling the reaction. A plot of initial rates against partial pressure of isobutylene indicated that the desorption of the products was definitely not rate controlling.

Since desorption of products, mass transfer, and diffusional effects were not rate controlling, the possibility of the adsorption of reactants and surface reaction between adsorbed molecules as rate controlling was examined. Writing the stoichiometric equation for the reaction as

$$C_4H_8 + O_2 \rightleftarrows C_4H_6O + H_2O$$

and following the usual procedure of derivation (*10*), neglecting the term $(P_{C_4H_6O})(P_{HO_2})/K$ since K (equilibrium constant) for the gas phase oxidation of isobutylene was very large ($\ln K > 20$), equations for various postulated mechanisms relating the rate of formation of methacrolein and water were derived (Table II) and tested for the best fit of experimental data.

The data was most satisfactorily correlated by mechanism VI, which assumes that the rate-controlling step is a surface reaction between

Table II. Rate Equations

	Type of Reaction
Mechanism I:	Surface reaction between adsorbed isobutylene and adsorbed oxygen, adsorption of isobutylene controlling.
Mechanism II:	Surface reaction between adsorbed isobutylene and oxygen in gas phase, adsorption of isobutylene controlling.
Mechanism III:	Surface reaction between adsorbed isobutylene and adsorbed oxygen, adsorption of oxygen controlling.
Mechanism IV:	Surface reaction between adsorbed oxygen and isobutylene in gas phase, adsorption of oxygen controlling.
Mechanism V:	Surface reaction between adsorbed isobutylene and adsorbed oxygen phase
Mechanism VI:	Surface reaction between adsorbed isobutylene and oxygen in gas phase
Mechanism VII:	Surface reaction between adsorbed oxygen and isobutylene in gas phase

strongly adsorbed isobutylene and gaseous (or very weakly adsorbed) oxygen. The adsorption equilibrium constant for methacrolein ($K_{C_4H_6O}$) was assumed to be the same as for isobutylene since a change in $K_{C_4H_6O}$ had little effect on the correlation. Though the numerical value of the adsorption equilibrium constant for methacrolein could not be estimated precisely, the best fit to the experimental data was obtained when $K_{C_4H_6O}$ was of the same order of magnitude as $K_{C_4H_8}$. The reaction rate for the oxidation of isobutylene to methacrolein has been satisfactorily expressed by the following equation:

$$r = \frac{\alpha K_{C_4H_8} P_{C_4H_8} P_{O_2}}{1 + K_{C_4H_8} P_{C_4H_8} + K_{C_4H_6O} P_{C_4H_6O}}$$

$$\ln \alpha = \frac{-12{,}100}{RT} + \frac{20.1}{R}$$

where

$$K_{C_4H_8} = \frac{22{,}800}{RT} - \frac{26.8}{R}$$

$$K_{C_4H_6O} = \frac{22{,}800}{RT} + \frac{26.8}{R}$$

Figure 6 shows the comparison between the experimental and predicted values with the rate equation for an oxygen/isobutylene ratio of 4 at 450° C. The solid lines in the figure refer to the curve predicted by substituting the values of α, $K_{C_4H_8}$, and $K_{C_4H_6O}$ in the rate equation derived above; the circles represent the experimental data.

For Various Mechanisms

Rate (r)

$$\frac{\alpha P_{C_4H_8}}{1 + K_{O_2} P_{O_2} + K_{C_4H_6O} P_{C_4H_6O} + K_{H_2O} P_{H_2O}}$$

$$\frac{\alpha P_{C_4H_6}}{1 + K_{C_4H_6O} P_{C_4H_8O}}$$

$$\frac{\alpha P_{O_2}}{1 + K_{C_4H_8} P_{C_4H_8} + K_{C_4H_6O} P_{C_4H_6O} + K_{H_2O} P_{H_2O}}$$

$$\frac{\alpha P_{O_2}}{1 + K_{C_4H_6O} P_{C_4H_6O}}$$

$$\frac{\alpha K_{C_4H_5} P_{O_2} P_{C_4H_8} P_{O_2}}{(1 + K_{C_4H_8} P_{C_4H_8} + K_{O_2} P_{O_2} + K_{C_4H_{60}} P_{C_4H_{60}} + K_{H_2O} P_{H_2O})^2}$$

$$\frac{\alpha K_{C_4H_8} P_{C_4H_8} P_{O_2}}{1 + K_{C_4H_8} P_{C_4H_8} + K_{C_4H_6O} P_{C_4H_6O}}$$

$$\frac{\alpha K_{O_2} P_{C_4H_8} P_{O_2}}{1 + K_{O_2} P_{O_2} + K_{C_4H_{60}} P_{C_4H_6O}}$$

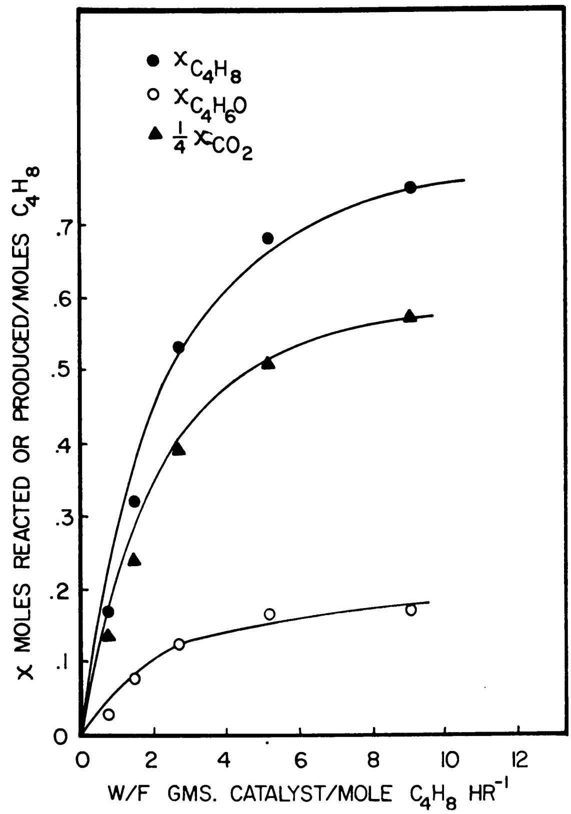


Figure 6. Conversion curve from rate equation and experimental data

Summary

The partial oxidation of isobutylene to methacrolein has been studied over supported and unsupported copper oxide catalysts, alone or mixed with other oxides in a flow reactor between 350° and 450° C. at atmospheric pressure for a W/F ratio of 0.12 to 16.8 and an oxygen/isobutylene ratio 0.25 to 4.0. The effect of various operating variables on the product has been discussed, and a rate expression for the reaction was determined.

Nomenclature

α = surface reaction rate constant combined with surface parameters
P = partial pressure, atm.
R = gas constant
N = oxygen (in air)/isobutylene ratio
K = adsorption equilibrium constant
T = ° K.

X = conversion, moles isobutylene reacted/moles isobutylene fed
y = yield, moles produced/moles isobutylene reacted
r = reaction rate

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Oxidation of Organic Compounds by Sulfur Dioxide under Pressure

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Alkyl substituted aromatic compounds are oxidized to the corresponding carboxylic acids by sulfur dioxide under pressure in the absence of catalysts or solvents. For example, toluene is oxidized to benzoic acid, xylenes to phthalic acids, and pseudocumene to trimellitic acid. The overall reaction may be represented by the equation: $RCH_3 + 1^1/_2\ SO_2 \rightarrow RCOOH + 1^1/_2\ S + H_2O$, sulfur and water being by-products. In the presence of excess sulfur dioxide, yields of 80–90% carboxylic acid may be achieved. The effects of reaction variables upon the reaction rate and yield have been studied. The reaction is catalyzed by compounds of bromine and iodine and inhibited by metallic copper and silver. Several other novel reactions of sulfur dioxide have been observed.

During an investigation into the reactions of sulfur dioxide with some simple organic compounds under pressure, several novel effects were found which, so far as is known, have not been reported previously. The most important is the oxidation of alkyl substituted aromatic compounds to the corresponding carboxylic acid by sulfur dioxide in the absence of both a solvent or a catalyst. The reaction may be illustrated by the oxidation of toluene to benzoic acid at temperatures around 250°–300° C. and a pressure of 300 atm: $C_6H_5CH_3 + 1^1/_2\ SO_2 \rightarrow C_6H_5COOH + 1^1/_2\ S + H_2O$ the coproducts being sulfur and water; the heat of reaction is —50 kcal./mole and the change in free energy is —34 kcal./mole. In the presence of excess sulfur dioxide, the conversion of the hydrocarbon is complete, and yields of 90% have been achieved. The reactions of sulfur dioxide with a wide range of organic compounds have been studied quali-

tatively, and the oxidations of toluene, xylenes, and pseudocumene to benzoic, phthalic, and trimellitic acids, respectively, have been studied quantitatively in much more detail. The purpose of this paper is briefly to review the experimental results derived from these studies.

Previous Work

The earliest oxidation effected by a sulfur compound was carried out by Willgerodt in 1887. He showed that aryl methyl ketones are converted to aryl acetamides by aqueous ammonium polysulfide (*26*).

$$\text{Ar—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—CH}_3 \xrightarrow[\text{(NH}_4\text{)}_2\text{S}_x 200^\circ\text{–}300^\circ\text{ C.}]{\text{Aqueous}} \text{Ar—CH}_2\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—NH}_2$$

The Willgerodt reaction has been widely studied and was reviewed in 1946 by Carmack and Spielman (*4*) who, in addition, indicated that early attempts to oxidize a saturated hydrocarbon side chain on an aromatic nucleus by aqueous polysulfide had failed. Subsequently, Toland at the California Research Corp. (*19*) and Naylor at duPont (*8*) found that under more vigorous conditions, alkanes and aralkyl hydrocarbons are oxidized to acid derivatives by a wide variety of sulfur compounds in aqueous solution. For example, Toland heated the hydrocarbon and sulfur compound together at 300° C. in the presence of a large excess of water at pressures around 170 atm. He used sulfur dioxide alone (*20*) or in conjunction with hydrogen sulfide, or an alkali or ammonium sulfite, or an alkali sulfide/sulfate mixture (*21*). In other processes, elemental sulfur has been used in water either alone or with a base (*22, 23, 24, 25*). Good yields are described for the preparation of benzoic and phthalic acids. It is likely that the oxidant in these reactions is water-soluble inorganic polysulfides (*10, 11*) produced by base-catalyzed disproportionation reactions of sulfur or sulfur anions. The mechanism of the reaction is reviewed by Pryor (*9*) who concludes that the effective species is the polysulfenyl radical and suggests the following scheme:

$$\text{Y}_2\text{S}_{a+b} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{YS}_a + \text{YS}_b \qquad \text{Y} = \text{H, Na, ArCH}_2\text{, etc.}$$

$$\text{YS}_a(\text{or YS}_b) + \text{ArCH}_3 \xrightarrow[\text{slow}]{k_3} \text{YS}_a\text{H} + \text{ArCH}_2\cdot$$

$$\text{Ar CH}_2\cdot + \text{YS}_a \xrightarrow[\text{fast}]{} [\text{Ar CH}_2\text{ S}_a\text{Y}]$$

$$[\text{Ar CH}_2\text{ S}_a\text{Y}] + \text{YS}_a \xrightarrow[\text{fast}]{} [\text{Ar CH}_2\text{ (S}_a\text{Y)}_2]$$

$$[\text{Ar CH}_2\text{(S}_a\text{Y)}_2] + \text{YS}_a \xrightarrow[\text{fast}]{} [\text{Ar CH}_2\text{ (S}_a\text{Y)}_3] \xrightarrow{\text{Rapid Hydrolysis}} \text{Ar CO}_2\text{H}$$

Strickland and Bell of Eastman Kodak (*17*) have oxidized toluene and xylenes with sulfur dioxide over vanadium pentoxide catalysts at atmospheric pressure. Toluene, at 410° C. with a contact time of five seconds, gave a conversion of 28% and 75% yield of benzoic acid while a lower temperature gave predominantly benzaldehyde. This method is not applicable to the preparation of phthalic acids; very low yields (less than 5%) were obtained presumably because these acids are not sufficiently volatile to leave the fixed bed reaction zone.

Experimental

For the preliminary qualitative experiments, high pressure reactors with a nominal capacity of 100 ml. were used which were lined with, or made of stainless steel and stirred by magnetically operated reciprocating stirrers. Heating was effected by an external, controlled electric furnace. Working with such small quantities of reagents to reduce the hazard, product recovery was poor, and it was not possible to derive meaningful reaction yields.

In more detailed quantitative studies of specific reactions, reactors of 1-liter and 25-liter capacity were used. The experimental arrangement was similar to the small reactors except that the 25-liter reactor was fitted with an internal cooling coil to assist in the control of the exothermic reaction.

The experimental procedure most commonly used was to charge a known weight of the organic compound to the reactor, assemble it into the furnace in a blast-proof reactor bay, heat to reaction temperature, and pressurize with sulfur dioxide. As the reaction proceeded, the pressure fell owing to sulfur dioxide's being consumed, and more was added intermittently from a compressor to maintain the reaction pressure. At the end of the reaction, the products could either be removed from the reactor by "blowing off" via a dip pipe at around 200° C. or by cooling the reactor, perhaps to —80° C., and dismantling. The best product recovery was obtained by the latter procedure.

For those carboxylic acids which are soluble in water, a simple water extraction was sufficient to give primary separation from the sulfur coproduct. Methods were developed to reduce residual sulfur contamination in benzoic acid and trimellitic anhydride, for example, down to the order of parts per million. For water-insoluble acids, it is necessary to avoid strong alkalis, such as caustic soda, which dissolve sulfur; extraction with sodium acetate solution was found to be applicable to terephthalic acid.

Example 1. Preparation of Benzoic Acid from Toluene. Into a liter reactor were placed 260 grams of toluene, heated to 300° C. and pressurized to 300 atm. by adding approximately 590 grams of sulfur dioxide. The reaction was completed in two and a half hours, during which a further 150 grams sulfur dioxide were added to maintain reaction pressure. The reactor was cooled, excess sulfur dioxide vented, and after drying the product weighed 469 grams. After extraction with water, 306 grams of benzoic acid were precipitated corresponding to a yield of 91% calculated on toluene.

Example 2. Preparation of Trimellitic Acid from Pseudocumene. In a similar experiment, 263 grams of pseudocumene and 700 grams of sulfur dioxide were heated together at 275° C. and 300 atm. During a reaction time of 11 hours, a further 200 grams of sulfur dioxide was added. 773 grams of dried product was obtained which, on extraction with water, gave 394 grams of trimellitic acid of approximately 94% purity, corresponding to a yield of 81% calculated on pseudocumene.

Sulfur dioxide is, in general, a good solvent for organic compounds; toluene, xylene, and pseudocumene are miscible in all proportions with sulfur dioxide. The reaction temperatures used for the oxidation reactions are above the critical temperatures of the binary phase, and the initial reaction at least is in the vapor phase. At the end of the reaction, the carboxylic acid is soluble in sulfur dioxide, and sulfur is insoluble. If the product of a reaction such as Example 1 were taken out of the reactor carefully, it was found to consist of two layers, the lower being mainly sulfur, containing about 5–10% benzoic acid and the upper layer containing about 85% acid. In the pure state the mutual solubilities in the molten systems benzoic acid/sulfur, trimellitic anhydride/sulfur are around 1% only.

Results

Exploratory Reactions. In general, only the more obvious results of these scouting experiments have been noted. In most cases, no attempt has been made to optimize the yield or study the reaction over a wide range of conditions.

Table I summarizes the results of reactions of sulfur dioxide with many different organic compounds. The oxidation of the methyl group substituted in an aromatic ring gives a high yield of the corresponding carboxylic acid in the presence of excess sulfur dioxide (*12*). If the methyl group is further substituted to ethyl or isopropyl (e.g., in cumene), the yield of benzoic acid is very reduced. As the number of methyl groups substituted in the benzene ring is increased, the yield of the carboxylic acid decreases as shown in Table II.

The rate of oxidation reaction is not affected by the addition of free-radical initiators or inhibitors, oxygen in small amounts, sulfur or inorganic compounds of sulfur. The reaction is catalyzed by bromine and iodine and their compounds (*13*), those containing bromine being the more effective. This will be discussed in more detail in this paper.

Benzaldehyde is oxidized to benzoic acid in good yield. The rate of this reaction is about 10 times as great as the oxidation of toluene under comparable conditions. This suggests that if the reaction proceeds via the aldehyde, the initial step is rate determining. If the oxidation of an aromatic hydrocarbon is stopped before completion, small amounts only of aldehydes may be found in the product.

The chlorotoluenes are oxidized to the acids, but nitrotoluenes are decomposed even under mild conditions. Yields of naphthalenecar-

boxylic acids were generally rather low. The activated methylene group in diphenylmethane was oxidized to a ketone. Phenol and naphthols did not react up to 300° C., but aniline decomposed with explosive violence with sulfur dioxide at 200° C.

Table I. Reactions of Organic Compounds with Sulfur Dioxide

Compound	*Temp., ° C.*	*Pressure, atm.*	*Product*
Toluene	250–400	50–2500	Benzoic acid 90% yield, dibenzyl, polybenzylidenes
Ethylbenzene	275	1000	Benzoic acid—moderate yield
Cumene	300	300	Benzoic acid—low yield
o-Xylene	275–300	1000	*o*-Toluic acid, phthalic acid
m-Xylene	300	300	*m*-Toluic acid, isophthalic acid
p-Xylene	250–320	100–500	*p*-Toluic acid, terephthalic acid 90% yield polyxylyenes
Mesitylene	275	1000	Trimesic acid
Pseudocumene	250–310	100–500	Trimellitic acid 80% yield
Durene	250	300	Pyromellitic acid, low yield
α-Methylnaphthalene	300	1000	α-Naphthoic acid
2,6- and 2,7-Dimethyl naphthalenes	280	300	Naphthalene mono- and dicarboxylic acids
Acenaphthene	300	300	Naphthalic acid
Tetrahydronaphthalene	250	300	Naphthalene
Decahydronaphthalene	250	300	Naphthalene
Dibenzyl	300	400	Benzoic acid
Stilbene	275	1000	Benzoic acid
Styrene	300	1000	Benzoic acid
Diphenylmethane	300	1000	Benzophenone
Methylcyclohexane	300	300	Benzoic acid
Cyclohexane	257	300	Diphenyl, sulfide, etc.
Cyclohexene	250	900	Diphenyl, sulfide, etc.
Benzene	450	900	Diphenyl, sulfide, etc.
Naphthalene	500	300	No reaction
Anthracene	500	300	No reaction
o-, *m*-, *p*-Chlorobenzaldehyde	275	300	Chlorobenzoic acids
o-, *m*-, *p*-Chlorotoluene	275	300	Chlorobenzoic acids
p-Dichlorotoluene	275	300	*p*-Dichlorobenzoic acid
Benzaldehyde	300	300	Benzoic acid, good yield
Cinnamic acid	300	1000	Benzoic acid
Benzyl alcohol	250	1000	Benzoic acid
Phenol	300	300	No reaction
α-Naphthol	275	1000	No reaction
Aniline	200	1000	Decomposition with explosive violence
Cyclohexanol	200	300	Adipic acid, low yield
Nitrobenzaldehyde	200	300	Decomposition
Nitrotoluene	200	300	Decomposition
2-Nitro-*p*-xylene	200	300	Decomposition
Pyridine	400	300	Addition compound pyridine—sulfur dioxide
α-Picolene	300	300	Addition compound picolene—sulfur dioxide
Ethylene	250	300	Polysulfone, sulfolane
Propylene	250	300	Polysulfone, methyl sulfolane
Butene	250	300	Decomposition
Decene	250	300	Decomposition
Ethylene oxide	250	500	Ethylene sulfite
Methyl-butyl alcohols	250	300	Ethers, good yields
Ethylene glycol	250	300	1.4 Dioxan
Acetic acid	300	300	No reaction

Table II

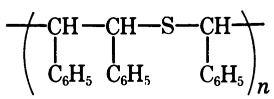
Hydrocarbon	*Product*	*Yield*	*Temp., ° C.*	*Pressure, atm.*	*Time, hrs.*
Toluene	Benzoic acid	>90%	300	300	3
p-Xylene	Terephthalic acid	90%	280	300	6
Pseudocumene	Trimellitic acid	80%	270	300	8
Durene	Pyromellitic acid	low	250	300	—

Unsubstituted aromatic compounds are comparatively unreactive to sulfur dioxide. Benzene reacted above 450° C. to give diphenyl, diphenyl sulfide etc., and naphthalene and anthracene did not react up to 500° C.

Neither pyridine nor picolines undergo oxidation or coupling reactions. Under milder conditions, a pyridine/sulfur dioxide addition compound is formed, and under more vigorous conditions extensive carbonization takes place. It is possible that the strong attraction between the aromatic nitrogen atom and sulfur dioxide precludes the possibility of attack at another part of the molecule. A similar result was obtained with pyridine hydrochloride.

Alicyclic compounds are, in general, dehydrogenated to aromatic compounds. This is a well known reaction of sulfur but has not previously been described for sulfur dioxide. Cyclohexane and cyclohexene gave diphenyl and diphenyl sulfides, similar to results described previously (5); methylcyclohexane gave some benzoic acid. Tetralin and decalin gave naphthalene. Cyclohexanol gave a small yield of adipic acid, this being the only case of those examined where an aliphatic acid was derived from a sulfur dioxide oxidation reaction.

For the oxidation of an aralkyl compound to the carboxylic acid to proceed to completion, it is necessary to maintain an excess of sulfur dioxide present. If the hydrocarbon is present in excess over sulfur dioxide, oxidative coupling through the methyl groups takes place. For example, dibenzyl was formed from toluene and compounds of high molecular weight (up to ~600) which were probably polybenzylidines containing sulfur links:



The reaction of xylenes with sulfur dioxide gave polyxylylenes. For example, from *p*-xylene low molecular weight polymers were formed which contained a molar ratio of about 6:1 xylene to sulfur. These are well known reactions of sulfur, but they have not previously been described for sulfur dioxide.

Other novel reactions of sulfur dioxide have been found which, while not oxidation reactions, are of interest.

ETHYLENE. It is well known that ethylene will copolymerize in excess sulfur dioxide in the presence of a free radical initiator to form ethylene polysulfone $(-CH_2-CH_2-SO_2)_n$ *(16)*. If an excess of ethylene over sulfur dioxide then is used with a free radical initiator, a small yield of sulfolane (tetramethylene sulfone) is obtained *(14)*. Propylene behaves in a similar manner. Attempts to oxidize propylene and isobutene to acrolein and acrylic acid derivatives were unsuccessful in both batch and continuous flow reactions.

OLEFIN OXIDES. Sulfur dioxide will react with olefin oxides in the presence of a base such as pyridine to form cyclic sulfites—e.g., ethylene sulfite—in good yield *(15)*.

ALIPHATIC ALCOHOLS. Ethers are formed in good yield by the reactions of the lower aliphatic alcohols with sulfur dioxide presumably by a reaction analogous to that with sulfuric acid. Ethylene glycol is converted to 1.4 dioxan.

To summarize, it has been found that sulfur dioxide may react in the following ways with organic compounds:

1. To oxidize an alkyl substituted aromatic compound to the corresponding carboxylic acid.
2. To bring about oxidative coupling of alkyl substituted aromatic compounds and benzene.
3. To dehydrogenate or aromatize alicyclic compounds.
4. To form cyclic sulfones with olefins.
5. To form cyclic sulfites with olefin oxides.
6. To form ethers from aliphatic alcohols.

Oxidation of Alkyl Substituted Benzenes. The reactions of most commercial interest were those leading to the simpler aromatic acids. The oxidations of toluene, xylenes, and pseudocumene to benzoic, phthalic, and trimellitic acids have been studied in some detail. The object of this work was to determine the effect of the reaction variables upon the rate and product yield and hence find the optimum conditions. This section summarizes the detailed results obtained. Kinetically, the three reactions are similar; where apparent differences were found, they could be related to the different heats of reaction—about 50 kcal./mole per methyl group. The oxidation of pseudocumene was studied in most detail up to a reactor size of 25 liters, toluene and xylenes being studied up to a reactor size of 1 liter.

A typical reaction was carried out as follows. The reactor was charged with reactants and brought to the required temperature and pressure as quickly as possible. When the reaction began, the pressure fell owing to consumption of sulfur dioxide, the pressure was allowed to fall, say 5–10%, the pressure drop measured and then restored by adding more sulfur dioxide from a compressor (Figure 1(A)). In this way an integrated pressure drop *vs.* time curve can be plotted (Figure 1 (B)). For

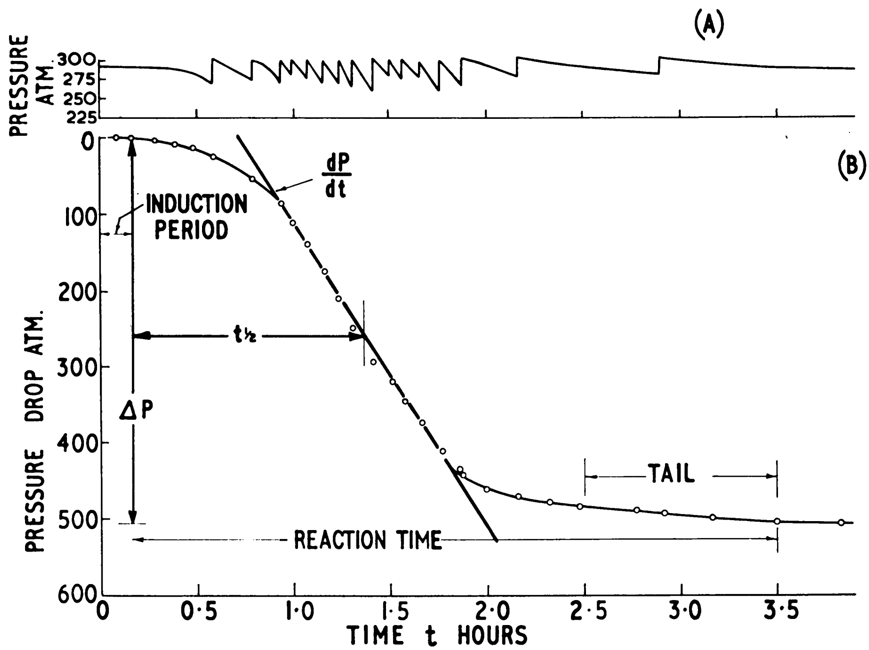


Figure 1. (A) Pressure curve; (B) Pressure drop curve for typical pseudocumene-SO_2 reaction

comparison, either the slope of the (nearly) linear portion of the curve dP/dt divided by the total pressure drop ΔP, or the time for half the pressure drop to occur, the time of half-change $t_{1/2}$, have been used as measures of the reaction rate. In some experiments, particularly in the smallest reactor, an induction period was sometimes observed but this rarely happened in the larger reactors. The "tail" on the curve was thought to be caused by the final stages of the reaction's taking place in a more viscous medium.

Effect of Reaction Variables upon the Rate. TEMPERATURE. The activation energies for the oxidation of toluene, xylenes, and pseudocumene are all within the range 42 ± 2 kcal./mole (*see* Figure 2, for example).

CONCENTRATION. The overall reaction rate is approximately proportional to the square of the hydrocarbon concentration (*see* Figure 3, for example).

PRESSURE. The reaction rate decreases with increasing pressure. Some results for a fixed weight of pseudocumene are summarized in Table III.

In these reactions the pressure is generated by compressing sulfur dioxide into the reactor, and an increase in pressure corresponds to a reduction in the mole fraction of the hydrocarbon. It has already been

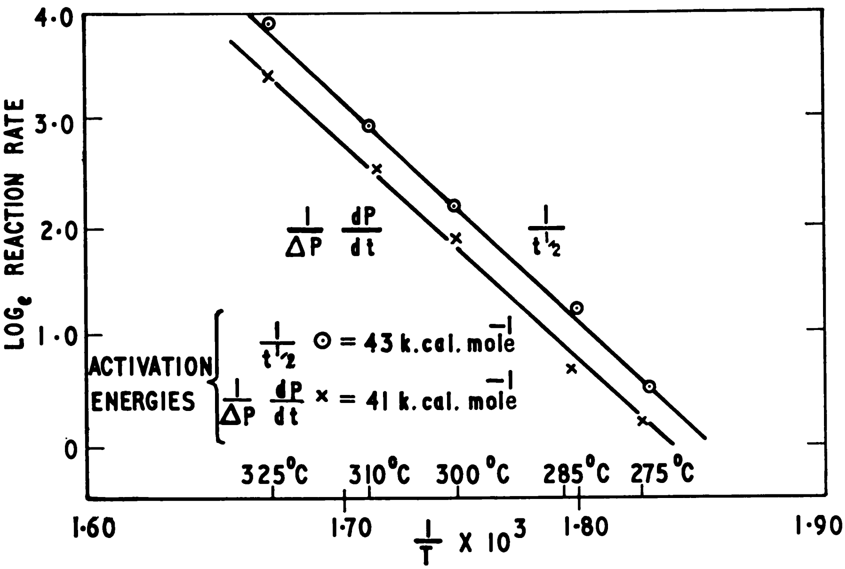


Figure 2. Arrhenius plots for oxidation of pseudocumene

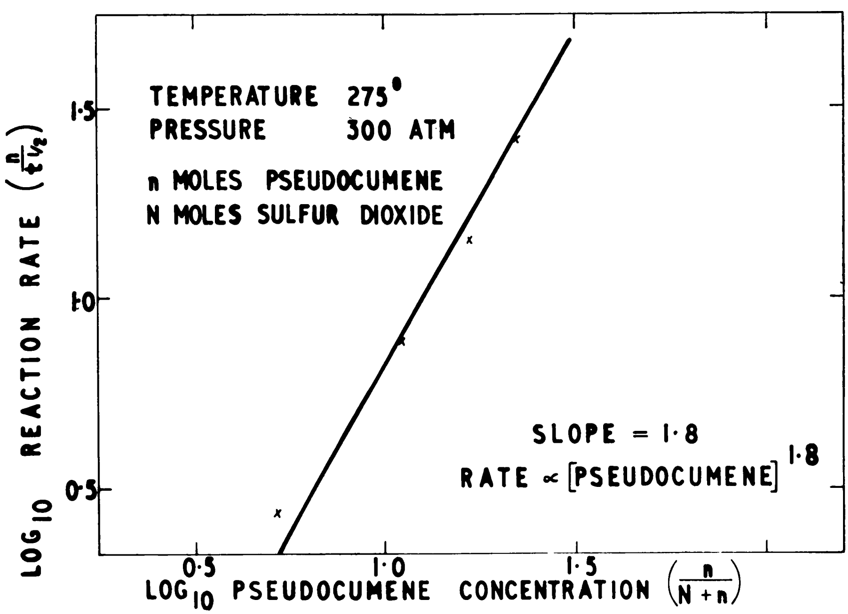


Figure 3. Effect of pseudocumene concentration on reaction rate

Table III

			Ratio of Reaction Rates		
Pressure, atm.	*Pseudocumene, mole fraction*	*Reaction rate $1/t_{1/2} \times 10^2$*	*Observed*	*Concentration Effect (Calculated)*	*Net Pressure Effect*
200	0.170	2.27	1.0	1.0	1.0
300	0.157	1.51	0.67	0.85	0.79
400	0.148	1.25	0.55	0.76	0.72

stated that at a given pressure the reaction rate is proportional to the square of the hydrocarbon mole fraction, and a correction must be made for this. In Table III, the ratios of the observed reaction rates may be compared with those expected from variation in concentration. The observed decrease in rate is greater than could be accounted for by a concentration change, indicating that there is a net retarding effect caused by pressure.

PURITY OF REACTANTS. Experiments have been carried out using commercial and specially purified samples of each reactant, but neither the reaction rate nor the product varied significantly with the purities of the reactants.

ADDITIVES. The reaction was not affected by the presence of a few atmospheres (say 5 atm. in 300 atm.) of oxygen or air. In the search for possible catalysts, many compounds were found to be without effect, for example, free radical initiators and inhibitors, metal salts (sulfates, sulfites, sulfides of alkali and transition metals), metal oxides, and chlorine compounds.

The reaction is completely inhibited by the presence of metallic silver or copper. For example, the reaction would not proceed in a 100 ml. reactor which was either lined with silver or had a silver stirrer. When small pieces of silver were added to a 1 liter reactor and a reaction carried out, there was initially a very long induction period after which the reaction proceeded at the rate appropriate to the conditions used. Silver sulfide was recovered from the product. Copper was found to behave similarly. It appears that these metals inhibit the reaction, but the metal sulfides do not.

The reaction is catalyzed by compounds of bromine and iodine, a small catalyst concentration giving a large increase in rate (Figure 4). Catalysis by 1% HBr (calculated on the hydrocarbon) has been shown to lower the activation energy from 42 kcal./mole to about 21 kcal./mole, and the increase in rate is proportional to log [HBr] (Figure 5). Both organic and inorganic compounds of bromine and iodine have been found to catalyze the reaction, the effect of bromine compounds being generally greater than that of iodine. It is well known that the bromine atom is able to abstract a hydrogen atom from a methyl group substituted onto an aromatic ring:

$$RCH_3 + Br\cdot \longrightarrow RCH_2\cdot + HBr$$

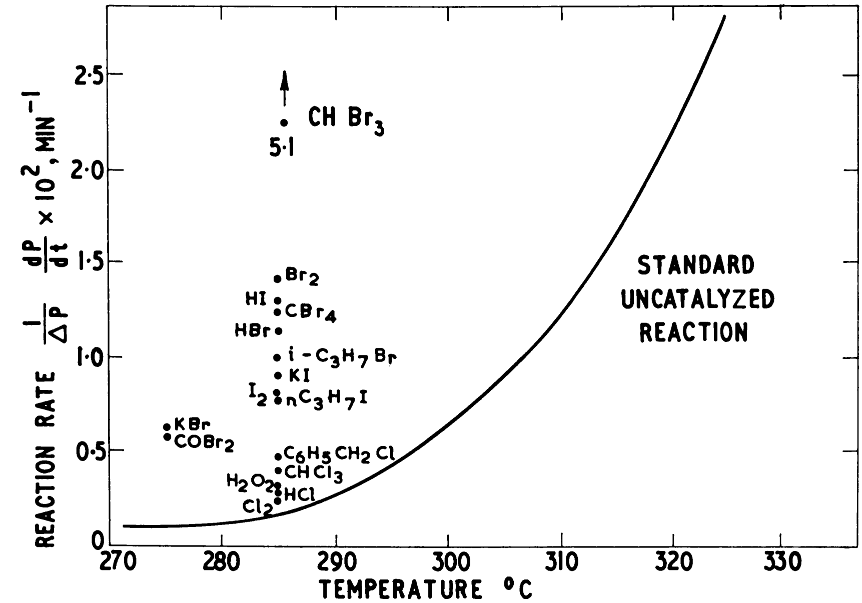


Figure 4. Effect of additives upon reaction rate (80 ml.)

Such a mechanism could account for the lowering of the activation energy of the overall oxidation reaction by catalysis of the initial step. Chlorine compounds are ineffective as catalysts because of the high redox potential required to form chlorine atoms.

SOLVENTS. It was thought that introducing a solvent to act as an inert diluent might help the reaction by reducing the viscosity in the latter stages and hence, aid mixing. Experiments were carried out with benzene, acetic acid, and water. The quality of the product was not significantly improved, and thus solvents were not generally used. With water and acetic acid, very heavy corrosion of the stainless steel reactor took place. In the absence of additives, the reaction mixture attacks stainless steel (18.10.Mo.Ti.) at a rate of about 0.1 inch per year under normal

Table

Volume of Reactor V, liters	*Radius of Reactor, cm.*	*Surface Area A / Volume cm.$^{-1}$*	*Ratio of A/V*
0.08	1.3	1.55	
			2.8
1.20	4.5	0.56	
			1.3
25.0	9.5	0.72[a]	

With cooling coil.
Uncooled (estimated).

reaction conditions. Addition of hydrogen bromide considerably increases corrosion.

REACTOR SIZE. This topic is relevant to the general problem of scaling up the size of the reactor. Table IV summarizes some results.

The three reactors were roughly similar geometrically; the one of 25-liter capacity was fitted with an internal cooling coil. The degree of agitation was comparable in each. All had reciprocating stirrers which were slow and rather inefficient, and it is assumed that the effect of the stirrer on the temperature distribution in each vessel is similar.

The maximum operating temperature is that at which it would just be possible to carry out a reaction at a controlled rate for a maximum charge

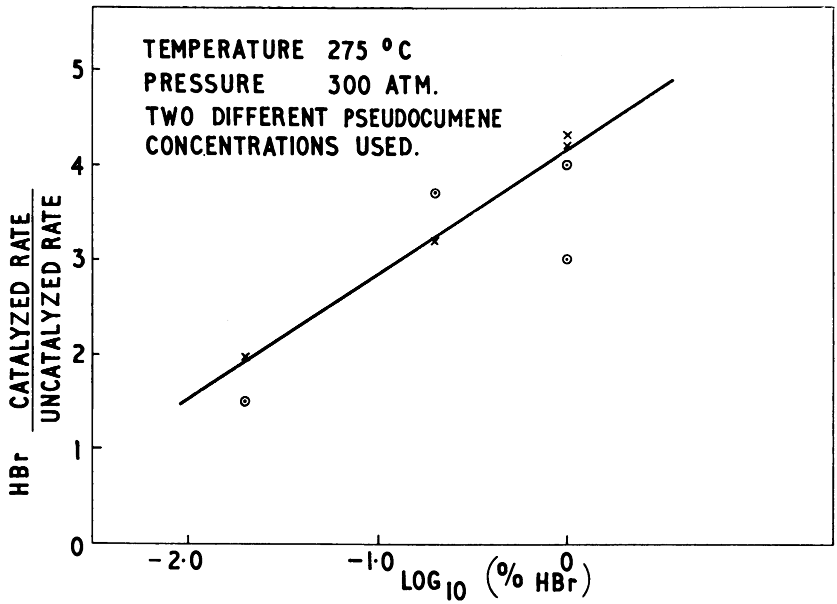


Figure 5. Effect of HBr catalyst concentration on reaction rate

IV

Maximum Operating Temperature, ° C.	*Time of Half-Change 285° C. min.*	*Ratio of Reaction Rates*	*Time of Half-Change 285° C., min.*	*Ratio of Reaction Rates*
310	260		115	
		2.3		1.7
280	113		70	
		1.1		1.3
290[a]	122		91	
250[b]				

of pseudocumene. The temperature measured corresponds approximately to that of the reactor wall, T_0. There is a clear relationship between this temperature and the reactor radius as shown in Figure 6. At the maximum operating temperature, the temperature distribution across the reactor is just on the point of becoming unstable because the rate of heat generation per unit volume by the reaction is greater than the rate at

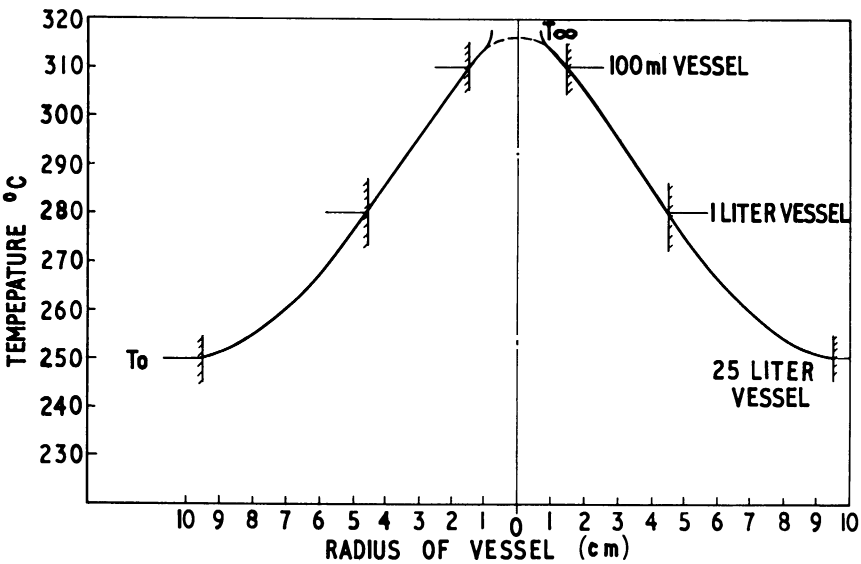


Figure 6. Temperature profile for 25-liter reactor with profiles for the smaller reactors indicated at maximum operating temperature

which heat can be lost by conduction to the vessel wall. The results given in Table IV show a relationship between the reaction rate and the surface area to volume ratio for the vessel. The heat of reaction causes the temperature within the reaction to be greater than at the reactor wall. A temperature distribution is established across the reactor similar to that shown diagrammatically in Figure 7. The observed reaction rate in each case will correspond to a temperature which is an average of T_1, the maximum temperature and T_0 the measured temperature. The rates will form a series such that:

$$\text{rate in 100 ml} < \text{rate in 1 liter} < \text{rate 25 liters uncooled}$$

The effect of cooling the 25-liter reactor with an internal coil is effectively to reduce T_0 as shown by the broken curve in Figure 7. This is why the measured rates in the 1-liter and cooled 25-liter reactors are similar.

In this context, it is of interest to compare the maximum operating temperatures of similar charges of toluene, *p*-xylene, and pseudocumene

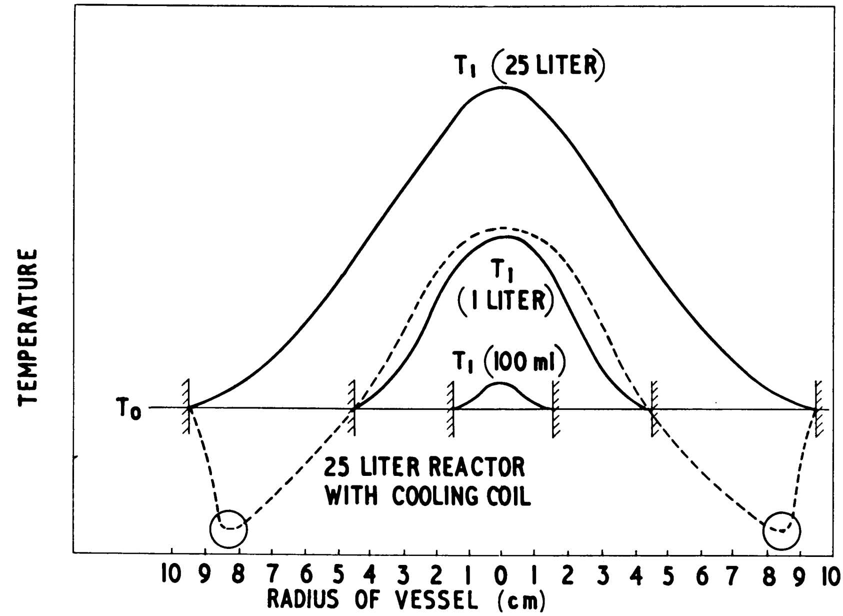


Figure 7. Increase in reactor internal temperature with increase in reactor radius; T_0 constant

in the 1-liter reactors. They were 335°, 310°, and 280° C., respectively, in the order expected from their increasing heats of reaction.

Much of the behavior of these reaction systems may be explained qualitatively on the basis of the Frank-Kamenetskii stationary theory of thermal explosion (*6*), particularly the effects of size of reactor, stirring, pressure, solvents, etc. upon reaction rate.

Product Yield. The yield from the sulfur dioxide oxidation reaction seems principally to depend upon the average reaction rate per unit volume. Figure 8 shows the variation of yield of trimellitic acid with reaction rate for pseudocumene in a 1-liter reactor. From this it can be seen that at rates below 10×10^{-6} gm.moles./ml. the yield may exceed 80% while at a rate higher than 30×10^{-6} gm.moles./ml./min., the yield may fall to 50%. Maximum yields in excess of 90% have been obtained for the oxidation of toluene and xylene.

The yield may be limited by the formation of intermediate compounds, tars, and degradation to carbon. Even in the presence of excess sulfur dioxide, when the reaction is apparently taken to completion, a small percent of intermediate acids may be present in the product. If the reaction is stopped before completion, then small quantities of aldehydes may also be found. The major by-product from *p*-xylene was *p*-toluic acid and from pseudocumene was 4-methylphthalic acid.

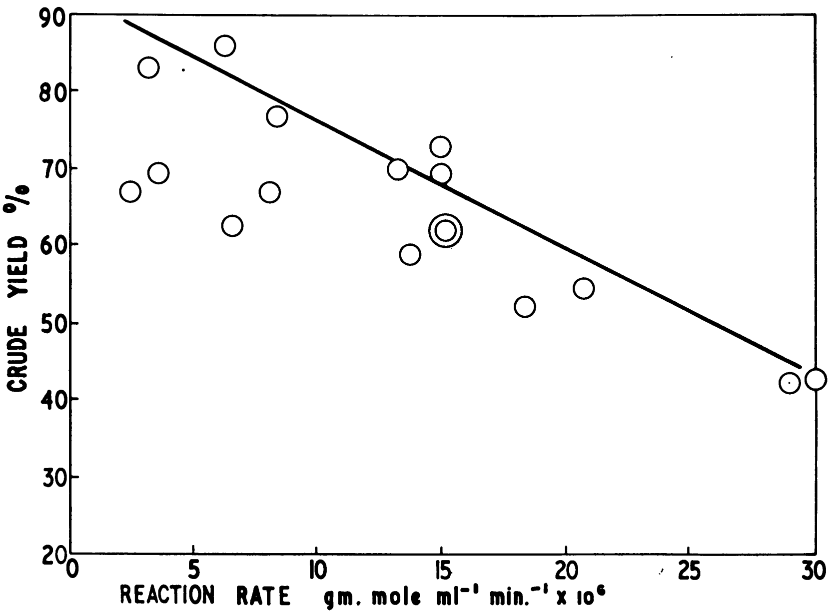


Figure 8. Variation of crude yield with reaction rate in 1-liter reactor

Degradation was not a serious problem in the 1-liter reactor, but it was a more serious problem from pseudocumene in the 25-liter reactor limiting the yield to about 75%. Formation of carbon in the product was accompanied by the formation of carbon dioxide in the gas phase. Small amounts of tarry materials were sometimes found in the products. From their infrared spectra and analyses, it seems likely that they were polymeric, having been formed by oxidative coupling reactions as described earlier.

Discussion

The primary objective of this work was to determine the optimum conditions for those reactions which might be commercially viable for manufacturing simple benzenecarboxylic acids. No serious attempt has been made to elucidate the mechanism of the reaction. Because initially the reactants are only sulfur dioxide and the hydrocarbon, it is unlikely that the reaction mechanism is identical to that for oxidation by alkali polysulfides in the presence of a large excess of water which was outlined in the introduction.

To summarize the experimental observations:

1. In the presence of excess sulfur dioxide the oxidation may proceed stoichiometrically according to Equation 1.

$$R \cdot CH_3 + 1^1/_2\, SO_2 \rightarrow R \cdot COOH + 1^1/_2 S + H_2O \qquad (1)$$

2. If the reaction is stopped before completion, aldehydes and hydrogen sulfide are found in significant quantities suggesting that the reaction proceeds via several steps such as:

$$R \cdot CH_3 + SO_2 \rightarrow R \cdot CHO + H_2O + S \qquad (2)$$

$$R \cdot CHO + {}^1/_2 SO_2 \rightarrow R \cdot COOH + S \qquad (3)$$

$$R \cdot CH_3 + SO_2 \rightarrow R \cdot COOH + H_2S \qquad (4)$$

$$H_2S + {}^1/_2 SO_2 \rightarrow 1^1/_2 S + H_2O \qquad (5)$$

The rate of oxidation of an aldehyde—Reaction 3—has been shown to be rapid compared with the overall Reaction 1, suggesting that the oxidation of methyl to aldehyde is the rate-controlling step. Reaction 5 is known to be fast.

3. In the presence of excess hydrocarbon, oxidative coupling reactions may occur.

$$2RCH_3 + SO_2 \rightarrow RCH_2CH_2R \text{ or } RCH_2SCH_2R \qquad (6)$$

4. The reaction appears to be homogeneous and not affected by surface catalysis.

5. The reaction rate is proportional to the square of the hydrocarbon concentration.

6. The reaction rate decreases with increasing pressure.

7. The reaction is catalyzed by bromine, iodine, and compounds of these elements.

8. The reaction is inhibited by silver and copper metals.

9. The reaction is neither catalyzed by standard free-radical initiators nor inhibited by standard free radical inhibitors (though it is possible that the catalysts and inhibitors used might have been inactivated by the reaction conditions used).

10. Attempts to oxidize olefins such as ethylene, propylene, butenes, etc. with sulfur dioxide so far have been unsuccessful. Any reaction other than an addition reaction, proceeded to carbonization. No more than traces of oxidation products have been found.

It is suggested that one possible reaction mechanism for this type of reaction is a free radical chain reaction based on the following scheme which is analogous to the accepted mechanism for the oxidation of hydrocarbon by oxygen (2, 3)

Initiation	$RCH_3 \rightarrow RCH_2\cdot + H\cdot$	(7)
	$(RCH_3 + x \rightarrow RCH_2\cdot + Hx)$	(8)
	$(RCH_3 + Br\cdot \rightarrow RCH_2 + HBr)$	(9)
Propagation	$RCH_2\cdot + SO_2 \rightarrow RCH_2SO_2\cdot$	(10)
	$RCH_2SO_2\cdot + RCH_3 \rightarrow RCH_2SO_2H + RCH_2\cdot$	(11)
	or $RCH_2SO_2\cdot + RCH_3 \rightarrow RCH_2SO_2CH_2R + H\cdot$	(12)
Termination	$RCH_2\cdot$, $RCH_2SO_2\cdot$ } Noninitiating or propagating products	(13)

Subsequent reactions $RCH_2SO_2H \rightarrow RCOOH + H_2S$ (14)

$$RCH_2SO_2CH_2R \rightarrow 2RCHO + H_2S \quad (15)$$

$$RCHO + {}^1/_2SO_2 \rightarrow RCOOH + S \quad (16)$$

It is known that hydrogen abstraction reactions are catalyzed by bromine (Reaction 9). Indeed, this forms the basis of the bromide-catalyzed air oxidation process (*7*), and the benzyl radical so formed is stable (*18*). The probability of forming benzyl radicals by thermal dissociation (Reaction 7) at around 250–300° C. is very low, and it is more likely that in the absence of a halogen, a sulfur species designated by x in Equation 8 is responsible. Absorption of x by copper or silver could cause the inhibition of the reaction. It is unlikely that elemental sulfur is the initiator because the addition of sulfur to the reactants did not affect the reaction rate. It may be noted that the initiation step may involve a net increase in volume and may be retarded by an increase in pressure.

Sulfur dioxide will copolymerize with olefins in the presence of free radical initiators to form 1:1 copolymers (*16*). For example, ethylene polysulfone $(-CH_2-CH_2-SO_2-)_n$ may be prepared under conditions similar to those used for aromatic oxidations. At higher temperatures, the polysulfones decompose to the olefins and sulfur dioxide. The reaction between styrene and sulfur dioxide proceeds differently (*1*). The primary product is a 1:1 complex $C_6H_5CH_2CH_2SO_2\cdot$ which then copolymerizes with another styrene molecule and not sulfur dioxide. The resulting polysulfone contains a 2:1 molecular ratio of styrene:sulfur dioxide. On the basis of this, the addition of a benzyl radical to sulfur dioxide and the subsequent reaction with the hydrocarbon is postulated (Reactions 10, 11, 12).

The subsequent rearrangement of the sulfinic acid or diaryl sulfone may occur to give oxidation products with a net increase in volume—Reactions 14 and 15—reactions which again might be retarded by an increase of pressure.

On the basis of experimental evidence so far available, it is not possible to propose such a reaction mechanism as anything more than a tentative hypothesis. In a full analysis, the contributions to the reaction of all the species present at various stages such as sulfur, hydrogen sulfide, organic intermediates, and less stable compounds would all have to be taken into account.

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6

Selectivity in the Liquid Phase Autoxidation of Olefins

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Selectivity in the liquid phase autoxidation of olefins is determined by the influence of structure on the elementary abstraction and addition reactions. Epoxides, as well as hydroperoxides, are considered to be primary reaction products because of their detection at very early reaction stages and the stereochemistry of their formation. *Cis*- and *trans*-2-butene and 4-methyl-2-pentene produce mixed epoxides richer in the trans isomers. While the unrearranged hydroperoxide from trans olefin is produced with retention of geometric configuration, the production of trans hydroperoxide is favored from cis olefin. The isomeric 4-methyl-2-pentenes show additional differences in behavior owing to the low reactivity of the tertiary hydrogen of the cis isomer.

The nature of the products and the mechanism by which they arise when oxygen reacts with unsaturated compounds has long been a subject of investigation in several areas in chemistry. The oxidation of olefins with molecular oxygen is involved in subjects as diverse as the degradation of polymers and the biogenesis of epoxides (*11*). The information reviewed here stems from an interest in petrochemicals and concerns the relationship of olefin structure to products and the steric course of the oxidation of cis and trans isomers.

The products obtained when liquid olefins react with oxygen may be divided into two categories: (1) the primary products produced in free radical propagation steps which require the consumption of oxygen and, (2) the secondary products which are produced by subsequent ionic and

radical reactions of the initial products. Primary products may be recognized by their failure to be influenced by other than drastic changes in reaction conditions, by their formation at very early stages in high total selectivities, and by the eventual appearance of predictable secondary products. Hydroperoxides have long been known as oxidation products which fit these criteria (*14*). Epoxides have only more recently been found to fit equally well (*7*), their description as primary products being supported also by the stereochemistry of their formation. A third product, whose occurrence is only suspected for nonconjugated olefins, is the polyperoxides (*10*). Whatever control is possible in influencing the yields and selectivities to end products in oxidations is generally directed towards preserving these products and modifying secondary reactions.

Relationship between Primary Products and Olefin Structure

Figure 1 depicts the relationship between primary products and the nature of the olefin. Examining the olefins shown and the relative yields of primary products emphasizes the importance of steric factors. Cyclohexene and the unconjugated 1,5-cyclo-octadiene produce high yields of hydroperoxide, resembling cumene in this respect. The amount of

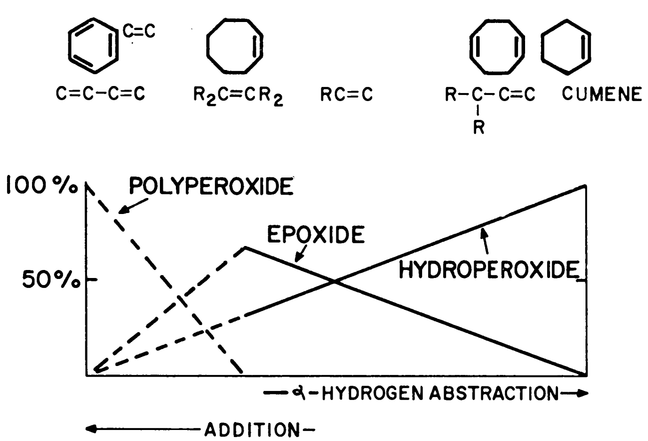


Figure 1. Relationship of structure to products

epoxide produced by oxidizing cyclohexene varies from about 3% at low conversions to a maximum of 12% at high conversions. Epoxide has not been identified in the oxidation products of the unconjugated cyclo-octadiene, and iodometric titration indicates that most of the oxygen reacted may be accounted for as hydroperoxide at low conversion. On the other hand, *cis*-cyclo-octene, which has a more strained ring and less favorable geometry than cyclohexene and presumably cyclo-octadiene, produces epoxide in yields up to 65% of olefin reacted. It should be

pointed out that all three compounds, representing epoxide yields ranging from 3% or lower to 65%, possess formally similar secondary allylic hydrogens, and perhaps all could have been expected to produce mostly hydroperoxide by reaction at this position. The differences in the relative activity of the α-hydrogen and the double bond are apparently enough to cause a major change in product distribution. When the overall oxidation rate of both eight-membered rings was determined and corrections were made on the basis of a second-order dependency for the larger number of active alpha positions in the diene, both olefins were found to have the same activity with oxygen. Thus, while the relative reactivity of the alpha position and of the double bond determine the primary product distribution, reaction at one site does not lead to an inherently faster rate than reaction at the other.

The acyclic olefins present wide differences in product distributions and interesting differences in oxidation behavior. Although epoxide yields, shown for the lower olefins in Table I, reflect the effect of subsequent ring openings as well as their ease of formation and therefore are dependent to some extent on conversion levels, it appears that olefins which may be oxidized to epoxides in the highest yields are, in general, the ones most substituted at the double bond. In many cases, a single aldehyde and its corresponding acid or ketone is produced in good yields from each olefin. The particular product may be anticipated by assuming oxidative fission of the double bond. Thus, 2-butene produces acetaldehyde, and 1-butene produces propionaldehyde. Although only the results for the *cis*-2-butene are shown, *trans*-2-butene yields essentially the same product results—approximately a 50% yield of epoxide and a high yield of acetaldehyde. While the *cis*- and *trans*-2-butenes show no significant difference in products or rates, the *cis*- and *trans*-4-methyl-2-pentenes show surprisingly large differences in the relative yields of epoxide and hydroperoxide obtained. For this reason, the behavior of these isomers was recently studied in detail, and the results will be discussed later.

Hydroperoxide yields obviously are much more dependent on conversion levels and reflect the accuracy of available analytical methods, which are always open to question. For this reason, no attempt was made to include them for all olefins in Table I which shows results obtained under practical synthetic conditions. The relative amounts of hydroperoxide and products formed by reaction at the double bond is important to olefin oxidation theory and has been the particular object of a recent study (*19*). Even at high conversions, however, when the olefin contains a tertiary allylic position, the formation of hydroperoxides are so favored that they may be identified or, as for 2-methyl-1-butene, isolated as the major product.

Table I. Effect of Structure in Olefin Oxidations[a]

Olefin	*Relative Rate* *Calc'd.*[b]	*Relative Rate* *Observed*	*Epoxide Yield, %*	*Other Products Yield, %*	*% Olefin Conversion*
C—C=C	0.5	<1	8	Methanol, 27	36
C C—C=C (C on 2nd C)	1.0	1.0	18	Acetone, 42	32
C=C—C—C	1.6	1.2	19	Propionaldehyde, 16	18
C C=C—C—C—C (C on 4th C)	1.6	1.4	21		38
C C=C—C—C—C (C on 2nd C)	2.1	2.1	24	2-Pentanone, 30	31
C C=C—C—C (C on 2nd C)	2.1	2.7	33	2-Butanone, 31	52
cis C—C=C—C	3.2	4.2	48	Acetaldehyde, 35	19
C C=C—C—C (C on 3rd C)	5.4	2.9	9	Hydroperoxide, 44	30
C C—C=C—C (C on 2nd C)	8.7	8.2	49	Acetone, 35	55
C *cis* C—C—C=C—C (C on 2nd C)	19.6	2.0	44	Hydroperoxide, 15	44
C *trans* C—C—C=C—C (C on 2nd C)	19.6	4.2	18	Hydroperoxide, 40	34
C C—C=C—C—C (C on 2nd C)	21.3	17	42	Hydroperoxide, 25	34

[a] In benzene, 50 mole %, at 120° C. and 300 p.s.i.g. oxygen. C_3, C_4, and C_5's from Brill and Barone (8).
[b] Using Bolland's rules for calculating "k_3" Bolland (5).

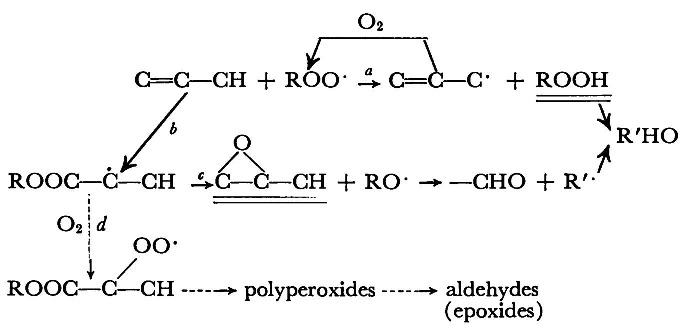
Effect of Structure on Reactivity in Autoxidations

The gross reactivity of olefins with oxygen may, in general, be correlated with structure using rules (5) originally intended to relate the ease of alpha hydrogen abstraction by molecular oxygen with the degree of alkyl substitution. For olefins containing primary or secondary allylic positions, the contribution of each position to the oxidation rate is increased by direct substitution at this position or at the unsaturated carbon furthest from it. Substitution at the adjacent unsaturated carbon has no effect. Olefins containing tertiary allylic positions and which tend to form mostly hydroperoxide appear to be abnormally unreactive when regarded from the standpoint of these rules (2, 8). Interestingly, an earlier study of the relative reactivity of amylenes (12) which followed the formation of hydroperoxide rather than the absorption of oxygen indicated that

3-methyl-2-butene was unusually reactive. The usefulness of an empirical method for predicting reactivity, even one limited to olefins without tertiary alpha hydrogen, is illustrated by the results reported in Table I for 2-methyl-2-pentene. Since the initially obtained rate was only one-tenth of that expected, continued purification of the olefin was indicated and led finally to the rate value reported.

Reaction Pathways

The contention that hydroperoxides, epoxides, and possibly polyperoxides are primary reaction products may be discussed in terms of the following mechanism (*8*):



After initiating radicals are formed by hydroperoxide decomposition, peroxy radical may react with olefin by either alpha hydrogen abstraction (*a*), or addition to the double bond (*b*). Abstraction results in the formation of an allylic radical which can react with oxygen to regenerate the same peroxy radical (or its allylic or cis-trans isomer). The net result of this propagating sequence, which has been studied in great detail (*14*), is to yield hydroperoxide, the exclusive primary product from saturated hydrocarbons, and the nearly exclusive product from olefins such as cyclohexene. When the double bond is sufficiently susceptible to reaction relative to the α-hydrogen, addition (*b*) as well as abstraction (*a*) takes place. The peroxy radical intermediate which is formed is capable of either forming epoxide directly (*c*) or reacting further with oxygen as shown (*d*). To explain the high epoxide yields obtained with the more substituted olefins (*7*), a reaction sequence involving decomposition of alkoxy radical was proposed. Subsequent reactions of the vinyl radical produced lead eventually to the production of additional epoxide and a ketone or aldehyde with one carbon less than the original olefin.

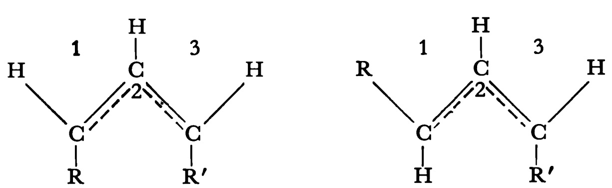
Reaction of the peroxy radical addition product with oxygen (*d*) was proposed by Mayo (*15*) for the oxidation of styrene and α-methyl styrene. It may be expected to be involved with nonconjugated systems,

but it is difficult to detect. However, it has helped explain the differences in the aldehyde products from 1-butene and 2-butene (*8*). The identical aldehydes or ketones may be produced from reaction routes (*a*) or from (*b,c*) which, incidentally, would make the experimental distinction between the two routes difficult when unstable hydroperoxides are produced. For the isomeric butenes, the particular aldehydes produced could not be explained easily by these mechanisms while decomposition of polyperoxide would be expected to produce the correct products. For other olefins, such as isobutylene which oxidized to acetone in a 42% yield, all three routes are able to lead to the same secondary products.

By regarding the peroxy radical as an electrophilic reagent or, alternatively, by examining the stability of the radical formed in each case, the general effect of substitution on both addition or hydrogen abstraction should be predictable. However, only when an alkyl group is substituted at the alpha carbon is abstraction favored exclusively. Substitution on the adjacent unsaturated carbon should favor only addition, but this assumption cannot be tested readily for the series of olefins studied since, besides experimental complications, the alkyl groups themselves introduce new reactive hydrogens. If addition occurs, the further course of the reaction appears to depend on the reactivity of the peroxy alkyl radical produced; the radical from mono-olefins form epoxide intramolecularly while the more resonance-stabilized radical from conjugated olefins survives long enough to react with oxygen.

Isomeric Products. Both the hydroperoxide and epoxide products formed from olefins may be expected to be found in isomeric forms. Hydroperoxides may be allylic position isomers and cis or trans geometric isomers, while epoxides may be cis or trans isomers. It was hoped that an analysis of the exact composition of products from a pure cis and trans olefin pair would clarify the factors controlling the steric course of oxidations. The oxirane ring always is produced at the position previously occupied by the double bond, and epoxide position isomers need not be considered.

In 1951 Knight, Eddy, and Swern (*13*) suggested that the radical produced by alpha hydrogen abstraction during the autoxidation of methyl oleate be represented by a resonance hybrid which can exist in one or the other of two isomeric forms.



Since maximum resonance energy is obtained when all three carbons and

their three hydrogen atoms lie in the same plane, neither form should be capable of free rotation. The infrared spectra of the oxidizing cis ester had shown a growing absorption band at about 10.3μ thought to be typical of a trans olefin and which was interpreted as indicating the formation of a mixture of methyl trans hydroperoxide octadecenoates. It was suggested that the majority of the radicals take the second configuration and that oxygen adds at carbon-3. The authors considered this explanation, involving the assumption that allylic radicals retain their configuration, as the most reasonable one to explain their results, but several alternative explanations were offered. The configurational stability of allylic radicals has subsequently been demonstrated for radicals produced during the chlorination of olefins with *tert*-butyl hypochlorite (*20*), and the stability of similar allyl carbanions and carbonium ions (*21*) has been postulated. Oxidations are believed to be good systems in which to demonstrate allyl radical behavior since their rapid reaction with oxygen results in a short lifetime and should not present much opportunity for isomerization to occur. The oxidation of both 2-butene and 4-methyl-2-pentene have now been studied.

Addition of peroxy radical to a cis or trans olefin also gives an opportunity for steric selection to occur. If the lifetime of the radical produced is very short, closure to the isomeric epoxide corresponding to the olefin occurs. If closure is slow and further reaction with oxygen does not occur, rotation will produce a mixture of cis and trans epoxides. The results actually observed with pure cis and trans olefins (Table II) indicate that rotation does occur but that some molecules seem able to form

Table II. The Oxidation of Olefin Isomers

		Hydroperoxide[b]						
	Epoxide[a]	*Hydrogen Abs.*			*Product Formed*			
	trans/cis	*prim.*	*sec.*	*tert.*	*prim.*	*sec.*	*tert.*	*trans/cis*
cis-2-Butene	1.5	all	—	—	53%	47%	—	1.8
trans-2-Butene	3.3	all	—	—	55%	45%	—	all trans
1-Butene	—	—	all	—	10%	90%	—	all trans
cis-4-Methyl-2-		54%			61%	39%		[d]
pentene	2			46%		48%	52%	5
trans-4-Methyl-2-		8%[c]			60%	40%		[d]
pentene	8			92%		57%	43%	all trans

[a] At conversions around 30% in 50 mol % benzene, (*8*).
[b] At very low conversions, butenes from (*16*).
[c] Maximum possible value.
[d] Not determined.

epoxide immediately. Thus, the formation of the more stable trans epoxide is always favored, but relatively more of the cis epoxide is produced from the cis olefin. It should be noted that the epoxidation of olefins by direct reaction with hydroperoxides is stereoselective (*9*) and must be considered for some cases, especially at high conversions, when interpreting the cis-trans epoxide ratio. Oxidation by hydroperoxide has

been recently assumed to be the sole mechanism by which configuration is retained for the isomeric methylpentenes, but the presence of a metal ion catalyst in this study (*1*) makes it seem less likely that this is correct.

Evidence for the formation of epoxide as a primary product is based on its appearance at very early stages of oxidation and on the fact that the only feasible secondary reaction which can produce epoxide—reaction of olefin with hydroperoxide—is found to be stereospecific and slow. To some extent, support is also supplied by the behavior of peroxy radicals generated by the oxidation of hydroperoxide with metal ions. The oxidation of methallyl chloride (*6a*), α-di-isobutylene, cyclohexene (*7*), *cis*-cyclo-octene, and *cis*-4-methyl-2-pentene all produce epoxide within reaction levels of around 0.1%. Extrapolation of epoxide and hydroperoxide concentration curves to zero time indicate that epoxide arises simultaneously with hydroperoxide. Analysis of the data from the early reaction stages indicates that if hydroperoxide interacts with olefin to produce epoxide, it must do so at a rate over 100 times faster than expected from separate rate studies of this reaction (*7*). The evidence is strongest for the oxidation of cyclohexene since cyclohexene hydroperoxide can be obtained relatively pure, and its decomposition in olefin has been carefully analyzed kinetically (*3*). The possibility exists that acyclic allylic hydroperoxides, especially those that are secondary and primary, may prove to be unusually reactive, but their isolation and study has not yet been accomplished. Studies to date have involved decomposition of the peroxide in crude oxidates, and under these conditions no epoxidation ability could be demonstrated for di-isobutylene hydroperoxide. Observed increasing epoxide yields with time appear to be real and indicate that in some cases at least a secondary reaction does produce epoxide.

From the ratios of trans to cis epoxide found in the products from the oxidation of the isomeric butenes and 4-methyl-2-pentenes to high conversions, it again appears that epoxide must arise by a mechanism other than stereospecific epoxidation with hydroperoxide. To test whether partial retention occurs owing to closure of the radical intermediate $ROOCRH\dot{C}RH$ to epoxide before rotation can occur, or owing to the direct epoxidation of olefin with hydroperoxide, the isomer ratio from 4-methyl-2-pentene is being studied at very low conversions. Thus far, it has been found that *cis*-4-methyl-2-pentene can produce relatively more cis epoxide during the induction period than is found at later stages of its oxidation.

The recent publications (*16*) on the oxidation of the butenes from the Laboratoire d'oxydation, Institut Français du Pétrole represent the most complete reported study of a lower olefin. The identity and distribution of the isomeric hydroperoxides from both butene-1 and butene-2 was determined by reducing the products from oxidations at 65° and

85° C. with lithium aluminum hydride to a mixture of the more stable allylic alcohols. The alcohols were characterized and analyzed by gas chromatography, infrared and nuclear magnetic resonance spectra, and chemical derivatives. It was first shown that the oxidation could be conducted to give quantitative yields of hydroperoxide. The product distribution shown in Table II indicates that 1-butene and 2-butene do not yield the same hydroperoxide mixture and substantiates our conclusion that their oxidation does not involve the same intermediate resonance hybrid (*8*). However, it is difficult to reconcile the particular products we obtained at the latter stages of the oxidation—propionaldehyde from butene-1 and acetaldehyde from butene-2—with the specific hydroperoxides reported. Just as disturbing, the apparent quantitative yields of hydroperoxides reported are incompatible with our suggestion that radical addition reactions are responsible for these product differences. It should be pointed out that the aldehyde products reported for the gas phase oxidation of the butenes have been attributed to the interaction of the double bond with oxygen in the propagation step (*17*).

Analysis of the geometric isomeric products indicated that the formation of trans hydroperoxide was favored. Conceding that the intermediate 2-butenyl radical from the cis olefin must retain its configuration, the French workers proposed that it is the peroxy radical formed by straightforward reaction with oxygen which isomerizes to the trans form.

Our initial interest in the oxidation products from the methylpentenes was based on their ready availability by several reported processes for dimerizing propylene. From the clearly different product distribution observed for the *cis*- and the *trans*-4-methyl-2-pentenes under practical synthetic conditions (Table I), a strong steric influence on the reaction course was indicated. Even at relatively high conversions, it is apparent that the trans isomer behaves normally, producing hydroperoxide and the modest yields of epoxide expected from a tertiary olefin. The more hindered cis isomer, on the other hand, gives epoxide yields more commensurate with those obtained from internal olefins not possessing tertiary hydrogen. Since one of the major difficulties in predicting the effect of structure on the relative amounts of addition and abstraction is the equally favorable influence of alkyl substituents on both reactions, it was hoped that a more detailed study would be useful.

The crude oxidation mixtures were treated with sodium sulfite or lithium aluminum hydride to reduce the hydroperoxide to the corresponding alcohols. Products were isolated by fractionation and purified by gas chromatography. It is interesting to note that the hydroperoxide was stable enough to be isolated in moderately pure form from the oxidation of the trans olefin, but that chromatography resulted in partial decomposition (as evidenced by a rise in the base line) with the detection of a single peroxide peak.

Identifying the products by interpreting their infrared spectra was, in general, unsatisfactory because of the lack of predictable absorption differences for the isomers. Interpretation of NMR spectra was more useful, with the exception of anamolies observed for the tertiary alcohols, but several products could not be purified in sufficiently large quantities to yield usable spectra. It was, therefore, necessary to prepare most of the possible alcohols by more unequivocal methods, usually the appropriate reduction of the corresponding acetylenic alcohol. The reaction of olefins with *m*-chloroperbenzoic acid was a convenient method of preparing epoxide (*18*).

From the hydroperoxides produced from trans-4-methyl-2-pentene (Table II), it appears that hydrogen attack by peroxy radical takes place exclusively or almost exclusively on the tertiary hydrogen. The allylic radical produced reacts with oxygen presumedly at both the tertiary and secondary positions—apparently with a preference for the secondary carbon to yield two major hydroperoxides. The tertiary hydroperoxide formed was entirely trans, no cis alcohol being detectable in the NMR or IR spectra of the reduced and isolated fractions.

cis-4-Methyl-2-pentene, on the other hand, behaves as though its tertiary hydrogen were unusually unreactive. From the distribution of hydroperoxides formed, it appears that both the tertiary and the primary allylic hydrogens may be abstracted. Two different allylic radicals (position isomers) appear to form, and oxygen shows a slightly different preference for reaction at tertiary, secondary or, in this case, primary carbon. The tertiary alcohols isolated are found to be a mixture of cis and trans isomers with only about one-fifth of the molecules retaining their cis configuration.

The formation of the trans hydroperoxide in the oxidation of the cis olefin is best explained by rotation of the highly strained allylic radical formed by abstraction of tertiary hydrogen. An alternative mechanism involving successive allylic isomerizations of peroxy radical or hydroperoxide is shown to be possible by the results of current studies with the isolated hydroperoxide (*6b*). Rotation must occur rapidly, before the radical can react with oxygen, which does not seem unreasonable. The loss in resonance energy involved must be far less than the commonly suggested value of 25 kcal. for the resonance energy of allyl and less than the 12 kcal. proposed for butenyl (*4*). The favored formation of epoxide from an olefin, in which steric effects have reduced the activity of a tertiary hydrogen to approximately that of a primary hydrogen while electronic effects favoring double bond addition remain important, emphasizes the appropriateness of the previously described mechanisms. Addition should also be directly favored to some extent by the relief of strain which occurs in the cis olefin on forming the intermediate radical by reaction of peroxy radical at the double bond.

Conclusion

It is to be expected that many problems relevant to the present work—e.g., those involving the identification of ketones as primary products—will be solved by applying present techniques for product identification and analysis. On the other hand, many experimental problems still prevent the adequate testing of autoxidation theory. Difficulties which seem especially pertinent are accurate analysis of unsaturated hydroperoxides, the measurement or calculation of dissolved oxygen concentrations in a dynamic system, and the more realistic use of kinetic analysis. It is to be hoped that the type of research described in this paper, which has necessarily been directed toward an understanding of the products found in liquid phase olefin oxidations, will provide some stimulus to solve these and other experimental obstacles and lead to a better understanding of autoxidations.

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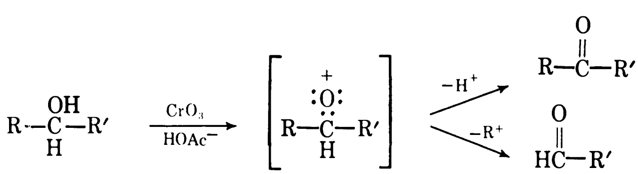
Oxidative Cleavage of Alcohols: Oxygen Effects

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Oxidation of *p*-substituted phenyl-*tert*-butylcarbinols with chromic acid gives data which correlates well with the Hammett relationship and cleavage yields as high as 60%. Manganous ion reduced both cleavage and the deuterium isotope effect. *p*-Substituents appear to have no effect on cleavage ratios. An induced air oxidation step has been detected during Cr(VI) oxidations of cleavable alcohols at high cleavage conditions. This step, however, is not responsible for the cleavage reaction. Oxidation yields are higher in the presence of oxygen, but the rates are lower. When phenyl-*tert*-butylcarbinol and *p*-anisyl-*tert*-butylcarbinol react with Fenton's Reagent, cleavages greater than those with chromic acid are obtained. Ce(IV) cleaves these carbinols almost quantitatively.

In 1944 we announced the discovery of the cleavage of highly branched secondary alcohols by chromic anhydride in acetic acid (*3*). Since that time, a series of papers has appeared from this laboratory showing this to be a fairly general reaction of secondary alcohols. The original hypothesis offered to explain this reaction involved the removal of hydride ion from the hydroxyl group by the action of the oxidizing agent, followed by electron pair rearrangement, resulting in either loss of proton to give ketone or loss of carbonium ion to give cleavage products. R^+ leads to ROH on reaction with water.



The work of Westheimer and his students on chromate esters (*2*) has left little doubt but that the formation of such esters precedes the oxidation step in chromate oxidations and that decomposition of the ester is involved in the rate-determining step of the reaction. The fundamental question is whether the normal oxidation and the cleavage reactions stem from a common process or whether they occur together. Because of the variation in cleavage obtained under different conditions, we favor the view that the two processes are simply different stabilization routes from a common intermediate as indicated above.

Westheimer's sequence of chromium oxidation states, the induced oxidation of Mn^{+2}, and the suppression of cleavage by Mn^{+2} would point to some chromium species other than Cr(VI) as the agent responsible for the cleavage reaction (*6*). The present work is directed at the question of a common intermediate or two separate routes. The cleavage of bornyl-*p*-tolylcarbinol to yield the acetate of isoborneol (*4*) and the cleavage of *l*-3-methyl-3-phenyl-2-pentanol to yield racemic-2-phenyl-2-butanol (*5*) offer rather convincing proof that the cleavage reaction is ionic in nature. The yield of cleavage varies within rather wide limits with changing acid concentration, also indicative of a polar mechanism. This concept is supported by the work of Watanabe and Westheimer (*6*).

To obtain additional information on the mechanism of the cleavage reaction, we prepared a series of *p*-substituted phenyl-*tert*-butylcarbinols (PBC) and oxidized them with chromic acid under various conditions.

Experimental Methods

Phenyl-*tert*-butylcarbinol and its *p*-chloro, *p*-fluoro, *p*-methyl, and *p*-methoxy derivatives were prepared by adding the appropriately *p*-substituted phenyl Grignard reagent to pivalonitrile. The products were purified by isolating the hydrochloride salts of the amines which were subsequently hydrolyzed to the ketones. The ketones were reduced to the corresponding alcohols with lithium aluminum hydride. 1-Deutero-1-phenyl-2,2-dimethylpropanol was prepared by lithium aluminum deuteride reduction of phenyl-*tert*-butyl ketone.

A rapid, accurate method was developed to determine quantitatively the product composition resulting from the chromic acid oxidation of the above alcohols in 86.5% acetic acid at 30° C. This method involved gas chromatographic analysis and relation of the integrated peak to mole fraction. Gas chromatographic separations were made with a packing at 10% Carbowax 20-M on Fluoropak. This material gave excellent separation of ketone, acid, aldehyde, cleaved alcohol, and unreacted carbinol.

Results

The data obtained have correlated very well using the Hammett relationship, and a negative ρ-value has been calculated for the Hammett curve (Figures 1 and 2). The cleavage percentages for the chromic acid oxidations of the substituted carbinols have also been determined.

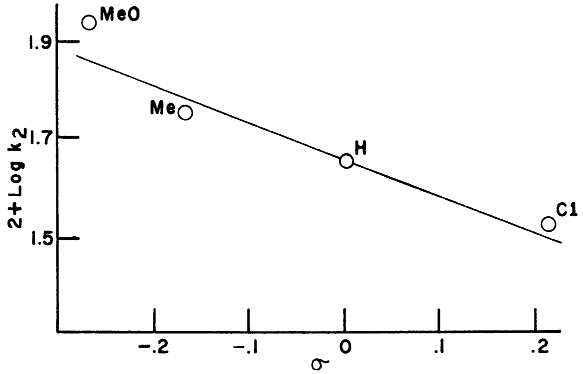


Figure 1. Log k_2 vs. the Hammett σ constant

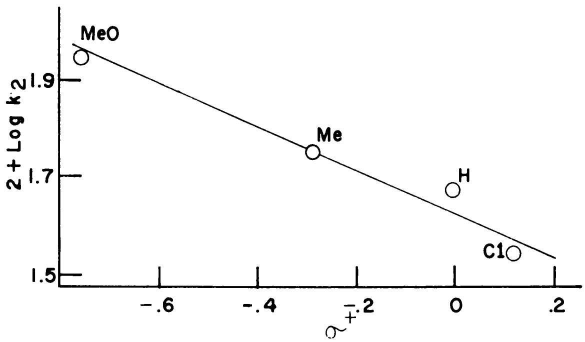


Figure 2. Log k_2 vs. the Hammett σ^+ constant

The cleavage fraction for the above alcohols was shown to be proton-concentration dependent (Table I). The cleavage reaction was also found to be reduced by the presence of manganous ion. Although cleav-

Table I. Addition of Oxidant at Constant Rate over One Hour

Temp., °C.	PBC[a] (moles/l.)	Cr(VI) (moles/l.)	Additive	Additive (moles/l.)	% Oxidation 1 hr.	% Oxidation 48 hr.	Cleavage Fraction (f) 1 hr.	Cleavage Fraction (f) 48 hr.
0	0.402	0.101			79	88	0.26	0.29
0	0.407	0.102	NaOAc	0.407	5	90	[b]	0.50
0	0.390	0.100	NaOAc	1.840	0	99	[b]	0.57
25	0.399	0.100			87	92	0.42	0.44
25	0.403	0.101	NaOAc	0.405	47	92	0.45	0.47
25	0.405	0.101	NaOAc	1.840	12	96	[b]	0.54
50	0.373	0.100			113	116	0.47	0.46
50	0.408	0.102	NaOAc	0.407	89	97	0.55	0.51
50	0.406	0.102	NaOAc	1.840	75	102	0.56	0.57

[a] PBC = Phenyl-*tert*-butylcarbinol; Solvent: 86.5% acetic acid.
[b] Peaks too small to measure accurately.

age fractions as great as 0.60 could be obtained, no cleavage fractions in excess of 0.67—the value suggested by Westheimer (*1*)—could be produced under the optimum conditions for high cleavage. The *p*-substituents were shown to have no effect on the cleavage fraction in the solvent used.

Chromic acid oxidation of phenyl-*tert*-butylcarbinol or *p*-anisyl-*tert*-butylcarbinol in the presence of acrylonitrile has led to the formation of polyacrylonitrile. This has provided evidence for the existence of free radicals during these oxidations, but attempts to identify the radicals have failed.

Adding manganous ion to Cr(VI) oxidations of *p*-anisyl-*tert*-butylcarbinol failed to eliminate the C—C fission products. However, it was found that the manganese dioxide, which forms during the reaction, is itself capable of oxidizing and cleaving the anisyl carbinol under the experimental conditions.

Both phenyl-*tert*-butylcarbinol and *p*-anisyl-*tert*-butylcarbinol reacted with Fenton's Reagent—a one-electron transfer oxidant—and cleavages greater than those obtained with chromic acid have resulted. These same carbinols have been cleaved to aldehyde almost quantitatively by Ce(IV) ion.

Effect of Nuclear Substitution on Cleavage Yield. A series of *p*-substituted phenyl-*tert*-butylcarbinols, which were oxidized by chromic acid under identical conditions, gave the cleavage yields below.

Carbinol	*% Cleavage No Additive*	*% Cleavage 0.05M NaOAc*	*% Cleavage 0.1M NaOAc*
p-H	23	38	44
p-MeO	30	38–45	50
p-Me	22	36	
p-Cl	22	43	

The percent cleavage of the *p*-methoxy compound rose to 66% as the sodium acetate concentration was increased to 2*M*.

Effect of Oxygen on the Rate of Chromic Acid Oxidations (*7, 8*). Kinetic values for the CrO_3 oxidation of phenyl-*tert*-butylcarbinol in 86.5% HOAc at 25° C. were determined for runs under air and under nitrogen. A difference in rates was detected, and a ratio of $k_{nitrogen}/k_{air}$ of 1.25 was calculated.

Effect of Oxygen on Product and Cleavage Yields. The results gathered from a number of comparable CrO_3 oxidations which were run under either air or nitrogen are listed below.

Chromic Acid Oxidations in the Presence of Acrylonitrile. When cleavable carbinols were oxidized by Cr(VI) in the presence of acrylonitrile, polymer formed. Blank runs demonstrated that the polymerizations were not initiated by the solvent, the oxidant, or action of the

products. No polymer appeared during oxidation of 2-propanol (non-cleaving).

Carbinol	Atmosphere	% Oxidation, Product Analysis	% Oxidation Cr(VI) Expended	% Cleavage
p-Anisyl-*tert*-butyl	Air	152[a]	100	45
p-Anisyl-*tert*-butyl	O_2	131[a]	100	42
p-Anisyl-*tert*-butyl	N_2	106[a]	100	54
Phenyl-*tert*-butyl	Air	70	76	22
Phenyl-*tert*-butyl	Air	72	61	33
Phenyl-*tert*-butyl	Air	91	85	42
Phenyl-*tert*-butyl	N_2	63[b]	73	50
henyl-*tert*-butyl	Air	60[b]	54	44

Slow addition of oxidant.
0.10*M* NaOAc.

Cleavage Yields in the Presence of Acrylonitrile. The following is a comparison of the cleavage yields attained in the presence of acrylonitrile, against those observed in its absence, from CrO_3 oxidations.

Carbinol	% Cleavage, AN Present	% Cleavage, No AN
p-Anisyl-*tert*-butyl	35	30
p-Anisyl-*tert*-butyl[a]	46	55
Phenyl-*tert*-butyl	37	42[b]

NaOAc Present.
Acetonitrile substituted for AN.

Solvent, Salt, and Light Effects. The cleavage percentages fluctuated only slightly as the solvent for the CrO_3 oxidations was varied from 60% to 95% acetic acid; however, when acetic anhydride-glacial acetic acid was used as a solvent, a 15% increase in cleavage occurred. Added neutral salts favored slight cleavage increases (0.377*M* $NaNO_3$, 7% increase). Variations in external light exposure (ultraviolet, darkness, and normal) failed to alter the aldehyde/ketone product ratio in Cr(VI) oxidations. Autoxidation of phenyl-*tert*-butylcarbinol under sunlight yielded principally benzaldehyde product.

Carbinol Cleavage by Fenton's Reagent. Fenton's Reagent readily oxidized *p*-anisyl-*tert*-butylcarbinol and phenyl-*tert*-butylcarbinol yielding high cleavage percentages (91% for the anisyl, 78% for the phenyl). As the concentration of HCl used in the oxidations was increased, the aldehyde product decreased. Di-*tert*-butylcarbinol was not attacked; pinacolyl alcohol gave only ketone product.

Carbinol Cleavage by Ce(IV). Pinacolyl alcohol, phenyl-*tert*-butylcarbinol, and *p*-anisyl-*tert*-butylcarbinol were cleaved almost quantitatively by ceric ion.

Kinetic Studies

In an effort to determine differences in the cleavage and oxidation reactions of Cr(V) with a cleavable alcohol, a series of *p*-substituted

phenyl-*tert*-butylcarbinols were oxidized. The data shown in Table II indicate that the cleavage fraction is independent of the *p*-substituent.

Table II

p-Substituent	*ROH (moles/liter)*	*Solvent*	*% Oxidation*[a]	*Cleavage*[a] *Fraction (f)*
H	0.412	A	88	0.55
Me	0.400	A	80	0.55
F	0.406	A	84	0.55
MeO	0.402	A	85	0.53
Cl	0.408	A	84	0.54
H	0.408	B[b]	90	0.22
MeO	0.413	B	81	0.20
F	0.417	B	88	0.21
MeO	0.409	B	88	0.22
Cl	0.410	B	86	0.20

Solvent: A—86.5% acetic acid; 1.00*M* sodium acetate.
B—86.5% acetic acid; 0.100*M* *p*-toluene- sulfonic acid.
(Cr) (IV) = 0.100*M*.
Temperature = 30.04° ± 0.04° C.
[a] Average of two runs.
[b] Reaction time of 1 hr. in solvent B.

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Kinetic studies were made of the oxidation of the alcohols in the absence and presence of manganous ion. The results were consistent with the mechanism previously proposed by Westheimer. Relative rate studies of phenyl-*tert*-butylcarbinol and its deuterated analog were also consistent with this mechanism. A relative rate, $k_H/k_D = 9$, was obtained for the overall reaction, and a deuterium effect of two was calculated for the oxidation by the proposed intermediate Cr(V) species. Competitive oxidations of phenyl-*tert*-butylcarbinol and its deuterated analog by chromic acid produced isotope effects in the absence and presence of manganous ion of 1.9 and 4.4, respectively. These values were also consistent with the proposed mechanism.

Application of the usual steady-state assumptions lead to the following expression:

$$v = \frac{-d(\text{ROH})}{dt} = K\,k_b\,(\text{HCrO}_4^-)\,(\text{ROH})\,(\text{H}^+)$$

This rate expression is similar to that used by Westheimer who followed the reaction by measuring the change in Cr(VI) concentration.

$$v = \frac{-d(\text{ROH})}{dt} = 2K\,k_b\,(\text{HCrO}_4^-)\,(\text{ROH})\,(\text{H}^+)$$

Discussion

It has been shown previously that a carbinol containing a tertiary α-carbon can undergo cleavage with the formation of a tertiary alcohol (3). The cleavage reaction presumably produces a stable tertiary car-

bonium ion which is then hydrolyzed to a tertiary alcohol. Two possibilities were presented as to the mode of removal of the hydrogen from the carbinol carbon in the first step (i.e., two-step hydride removal). These two possibilities must also be considered in the oxidation reaction by Cr(V) as suggested by the Westheimer mechanism.

If the C—C cleavage reaction proceeds with the formation of a carbonium ion and the C—H oxidation reaction were to proceed by way of a hydride removal, one would expect that electron-releasing substituents would favor the oxidation step owing to stabilization of the incipient carbonium ion created by hydride removal. Such a consideration would lead to a higher cleavage yield for compounds with electron-withdrawing substituents where the cleavage reaction would be favored. The fact that no difference in cleavage yields is observed leads to the conclusion that both the oxidation and cleavage reaction proceed by the same path (i.e., loss of a proton or tertiary carbonium ion) to form ketone or cleavage products.

An alternative mechanism should also be considered: if a free radical mechanism were operative, the oxidation and cleavage reaction could proceed by removal of a hydrogen atom or a tertiary alkyl radical. In such a case, the *p*-substituents would not be expected to influence the relative rates of the two reactions to any great extent. However, one would expect to observe isobutylene or 2,2,3,3-tetramethylbutane as the product of a free radical reaction. Attempts to isolate these products have been unsuccessful (Tables III and IV).

Table III

p-Substituent	*ROH* (*moles/ liter*)	*Cr(VI)* (*moles/ liter*)	k_2* (*moles/ liter*)$^{-1}$ *min.*$^{-1}$	k_3 (*moles/ liter*)$^{-2}$ *min.*$^{-1}$	k_X/k_H	*Cleavage Fraction* (*f*)
H	0.405	0.100	0.0187	70.0	...	55
CH_3	0.400	0.100	0.0193	72.3	1.03	55
F	0.409	0.100	0.0149	55.1	0.79	55
MeO	0.410	0.100	0.0271	100	1.43	53
Cl	0.402	0.100	0.0151	56.5	0.81	54

Temperature 30.04° ± 0.04° C.
Solvent: 86.5% acetic acid; 1.00*M* sodium acetate.
* Average of two identical runs.

On the other hand, the induced polymerization of acrylonitrile in the cleavage reaction points to some free radical formation in the process. This is the subject of continuing study. Actually, polymer yields were very low indicating low monomer conversion and presumably, low radical concentrations. Possibly the radicals are formed by a one-electron change in the Cr(VI) reduction. The high yields of cleavage, well above the 67% maximum required by the Westheimer mechanism, would indicate that the reaction with Fenton's reagent involves an entirely different type of

Table IV

-Substituent	ROH (moles/ liter)	Cr^{+6} (moles/ liter)	k_2 (moles/ liter)$^{-1}$ min.$^{-1}$	k_3 (moles/ liter)$^{-2}$ min.$^{-1}$	k_X/k_H	Cleavage Fracton (f)
H	0.401	0.100	0.00758	28.8	...	16
Me	0.408	0.100	0.00786	29.5	1.02	12
F	0.401	0.100	0.00659	24.7	0.86	14
MeO	0.412	0.100	0.0122	45.7	1.59	14
Cl	0.420	0.100	0.00595	22.3	0.78	10

Solvent: 86.5% acetic acid; 0.100*M* sodium acetate; 0.020*M* Mn^{+2}
Temperature 30.04° ± 0.04° C.

process, as would be expected, but that cleavage through a free radical mechanism is also possible.

The rather high oxygen effect coupled with the Fenton's reagent experiment might lead to the conclusion that cleavage occurs through a radical process. This conclusion is, however, not valid in view of the fact that oxygen has no effect on cleavage yield.

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8

2,6-Naphthalenedicarboxylic Acid and Other Aromatic Acids via Nitrogen Dioxide–Selenium Oxidations

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2,6-Naphthalenedicarboxylic acid and other potentially commercial aromatic acids can be produced by a novel oxidation process using nitrogen dioxide and selenium dioxide co-oxidants. The technique is of general interest in organic chemical manufacture since the method can be used to produce aromatic mono- and dicarboxylic acids, aldehyde oxidation intermediates, and quinones. Conversion of 2,6-dimethylnaphthalene to dimethyl 2,6-naphthalenedicarboxylate is typically accomplished, including esterification, with an overall yield of 85 mole %, and this process is described in detail. Major products and yields obtained from oxidation of other dimethylnaphthalenes, monomethylnaphthalenes, alkylbenzenes, and certain polynuclear aromatics are summarized.

As part of a general program on naphthalene chemistry, we have been interested in dimethylnaphthalene derivatives, particularly dimethyl 2,6-naphthalenedicarboxylate. This symmetrical diester not only has potential as a specialty chemical and intermediate but also could provide polyesters and polyamides with premium characteristics (*4, 6, 13*). These considerations triggered an investigation into the relatively unexplored chemistry of the dimethylnaphthalenes, particularly their oxidation.

All 10 dimethylnaphthalene isomers are present in varying concentrations in catalytic gas oils. The 2,6-isomer can be isolated from the gas oil in high purity and can be converted to dimethyl 2,6-naphthalenedicar-

* Carbogen Corp.

boxylate by processing steps previously outlined (*8*). The key step, however, is the conversion of methyl groups on the naphthalene nucleus to carboxylic acid groups. The following sections discuss this conversion in detail, outlining the known workable oxidation methods for dimethylnaphthalenes, specifically detailing the nitrogen dioxide-selenium method, and summarizing results obtained on oxidation of other organic substrates.

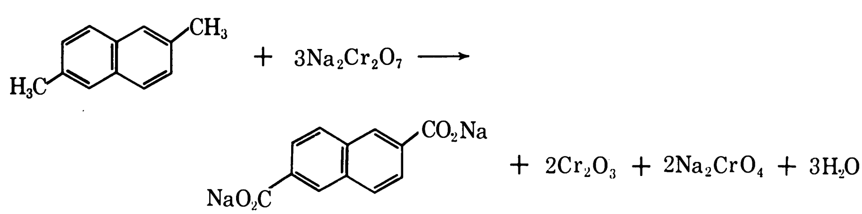
Oxidation Methods for Dimethylnaphthalenes

Our experience indicates that oxidation of dimethylnaphthalenes to dicarboxylic acids is more difficult to accomplish than oxidation of the corresponding dimethylbenzenes. Some methods which are quite adequate for oxidizing methylbenzenes are completely inadequate for oxidizing dimethylnaphthalenes. We may summarize the known, workable oxidation methods for dimethylnaphthalenes as follows:

The Sun Oil-Carbogen Process. This oxidation method, discovered and patented by L. J. Christmann and E. W. Roberts (*11*), produces 2,6-naphthalenedicarboxylic acid in good yield at 190–210° C., using nitrogen dioxide and selenium dioxide as co-oxidants, and trichlorobenzene solvent. The method is detailed in subsequent sections.

The Amoco–Mid-Century Process. This system is also capable of giving good yields of the desired naphthalenedicarboxylic acids. The reaction is typically accomplished at about 195° C. at 15–30 atm. with oxygen and cobalt and/or manganese salts and a bromide salt contained in acetic acid (*2, 12*). Although the method as patented describes oxidation at elevated temperatures and superatomspheric pressure, the method can be modified to produce oxidation at atmospheric pressure at temperatures blow 100° C., still retaining satisfactory reaction rates and yields.

The Aqueous Dichromate Method. This is an excellent laboratory method for producing naphthalenedicarboxylic acids in good yield and purity (*5*). The reaction is accomplished at 250° C. or greater, using aqueous sodium or potassium dichromate as oxidant. The reaction proceeds as follows:



Yields greater than 90 mole % are typical. Commercially, the process suffers from a serious disadvantage since the reaction is stoichiometric and requires several pounds of costly dichromate to produce a pound of naphthalenedicarboxylic acid.

The Sulfur-Ammonia-Water Method. A method claimed to give fairly good yields of acids from dimethylnaphthalenes involves oxidation of 2,6-dimethylnaphthalene in the presence of sulfur, ammonia, and water at 275° C. (*7*). This method produces approximately equal quantities of

mono- and dicarboxylic acids with total acid yields reported to be about 80 mole %.

Oxidation of 2,6-Dimethylnaphthalene Using the Nitrogen Dioxide-Selenium System

Experimental. Figure 1 illustrates the apparatus found to be quite effective for conducting the oxidation on a laboratory scale (9). The reactor C is a 3-liter resin flask equipped with stainless steel baffles and a triple turbine blade stirrer capable of 4500–5500 r.p.m. under reaction conditions. The reaction can be carried out in several ways. For example, in a typical batch process, a solution of 2,6-dimethylnaphthalene (200 grams) and selenium (2 grams) in trichlorobenzene (2000 ml.) is heated to reaction temperature (usually 195° C.). Nitrogen dioxide from tank A is passed through pre-heater B (150–190° C.) and introduced at the bottom of reactor C. The oxidation is continued until the exit gases show a definite brown coloration owing to unreacted nitrogen dioxide. Alternatively, dimethylnaphthalene contained in hot solvent can be added incrementally via a dropping funnel D. In this case, the oxidation of

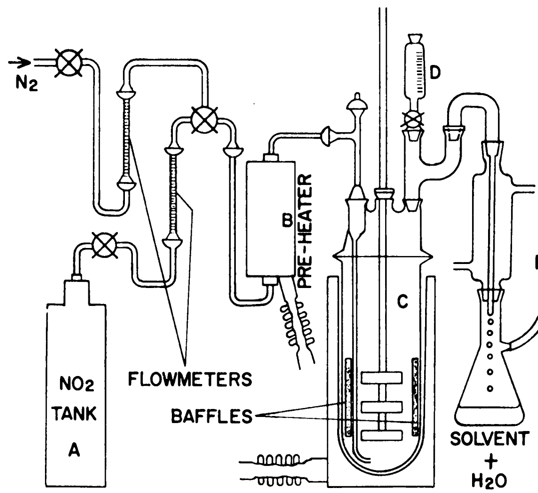


Figure 1. Diagram of laboratory oxidation apparatus

dimethylnaphthalene is conducted until the exit gases show a tinge of brown coloration, after which more dimethylnaphthalene is added. These additions are continued until all of the dimethylnaphthalene has been added to the reaction flask. In both procedures, nitrogen dioxide flow rate is approximately 2 grams per minute. After cooling the reaction mixture to room temperature under nitrogen flow, the contents of the reactor are filtered, washed with solvent, benzene, pentane, and finally dried. The reaction products are analyzed most reliably by quantitative esterification followed by gas-liquid chromatography. Alternatively, paper chromatography or neutralization numbers can be used.

Batch vs. Incremental Process. Table I summarizes results obtained for oxidations of 2,6-dimethylnaphthalene, with or without selenium, using the batch or incremental procedures (9) described in the preceding section.

Table I. Batch vs. Incremental Process for Oxidation of 2,6-Dimethylnaphthalene at 195° C.

	Mole % Yields		
Description	*2,6-NDCA*[a]	*6-F-2Na*[b]	*Total*
Batch process without selenium	43	15	58
Batch process with selenium	47	49	96
Incremental process without selenium	59	9	68
Incremental process with selenium	69	15	84

[a] 2,6-Naphthalenedicarboxylic acid (diacid).
[b] 6-Formyl-2-naphthoic acid (aldacid).

In the batch process, 2,6-dimethylnaphthalene is initially present at a concentration of 100 grams/liter. Higher concentrations favor formation of 6-formyl-2-naphthoic acid as the major product. Selenium is present at a concentration of 1 gram per liter, representing about half the maximum solubility of selenium at 195° C. Selenium dioxide is slightly less soluble at this temperature. Experience has shown that there is little gained by using increased quantities of selenium. It is clear from the data in Table I that without selenium the yield of acidic products is rather poor. Considerable nonacidic products are produced, including nitrated by-products. These complications are reduced with the use of selenium.

The temperature range for maximum conversion to acids at atmospheric pressure is 190–215° C. Lower temperatures result in undesirable nitration as well as decreased acid yields. The upper temperature limit is set by the atmospheric boiling point of the solvent, which in this case is 215°–217° C.

Pilot Plant Studies. A brief study of the incremental process was carried out in a small pilot plant. A 77 mole % yield of 2,6-naphthalenedicarboxylic acid was obtained. Work on this adaptation of the reaction was discontinued when it was discovered that better yields and purer product could be achieved by using a two-step oxidation process. From preceding data, it is clear that the batch process with selenium can be used to convert dimethylnaphthalene to an approximately equimolar mixture of diacid and aldacid. This is the initial step used as part of an overall scheme, shown in Figure 2, to produce dimethyl 2,6-naphthalenedicarboxylate. The process involves the following steps:

1. Batch oxidation (*A*) using selenium converts 2,6-dimethylnaphthalene to an approximately equimolar mixture of diacid and aldacid.

2. Esterification (3) of this equimolar mixture (*B*) using sulfuric acid and methanol produces the corresponding methyl esters.

3. Filtration of the cold reaction mixture isolates solids containing 95% dimethyl 2,6-naphthalenedicarboxylate. The methanol filtrate contains 95% 6-carbomethoxy-2-naphthaldehyde (aldester). Extraction of the methanol solution with trichlorobenzene (*C*) transfers the aldester into the trichlorobenzene, and this solution is subjected to further oxidation.

4. Oxidation of the aldester (*D*) is accomplished conveniently at 100° C. without selenium catalyst to give a good yield of 6-carbomethoxy-2-naphthoic acid. It should be noted that off gases from this oxidation contain appreciable quantities of unreacted nitrogen dioxide. These gases are fortified with additional nitrogen dioxide and used to carry out the primary oxidation (*A*).

5. Esterification of 6-carbomethoxy-2-naphthoic acid (*E*) gives the desired dimethyl 2,6-naphthalenedicarboxylate. Starting from dimethylnaphthalene, the overall diester yield is 85–90 mole %.

This process has been used successfully to produce over a ton of ester, which has been distributed to interested domestic and foreign companies.

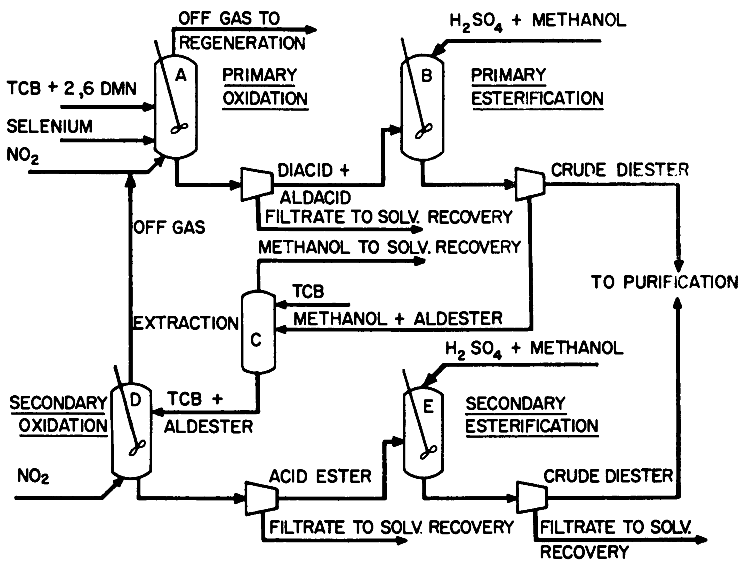


Figure 2. Process flow sheet for the oxidation of 2,6-dimethylnaphthalene

Rationalization of the Overall Reaction Path. The reactions involved in the nitrogen dioxide-selenium oxidation, shown schematically in Figure 3, can be rationalized by considering the following relative reaction rates at 195° C.

$NO_2 + Se \geq SeO_2 + DMN > NO_2 + Aldehyde > NO_2 + DMN >$ $SeO_2 + Aldehyde$. From this information we deduce that (under the proper conditions of selenium concentration, dimethylnaphthalene concentration and nitrogen dioxide flow rate) nitrogen dioxide will enter the reactor and be completely consumed by the rapid reaction with selenium. The resultant selenium dioxide is rapidly reduced back to selenium by reaction with dimethylnaphthalene, producing aldehyde as the initial product. This cycle is continuously repeated as long as unreacted dimethylnaphthalene is present. Simultaneously, the aldehydes produced

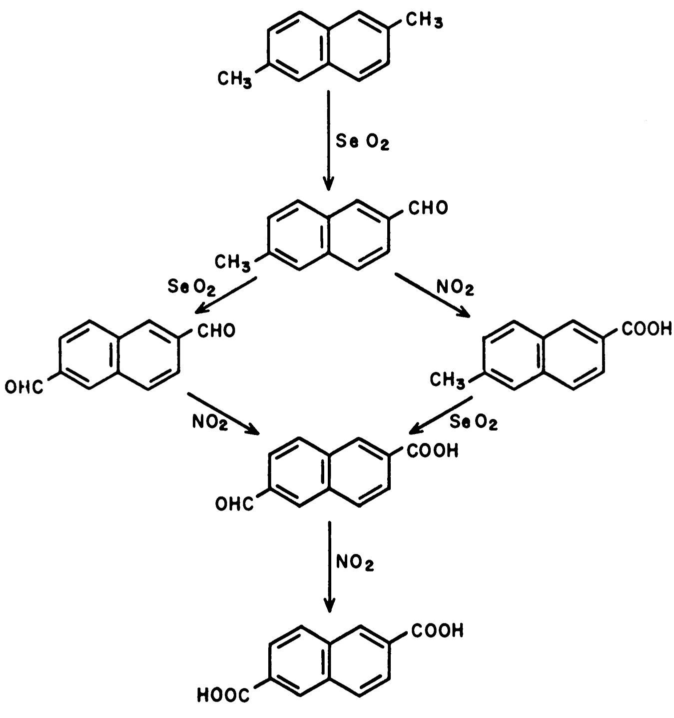


Figure 3. Nitrogen dioxide-selenium oxidation of 2,6-dimethylnaphthalene

will be converted to acids by reaction with NO_2. Thus, if a sufficient dimethylnaphthalene concentration is maintained, all of the nitrogen dioxide will be consumed and the effluent gases from the reactor will be colorless. As oxidation progresses and dimethylnaphthalene is consumed, more nitrogen dioxide will be available to convert aldehydes to acids. Ultimately, as the acid concentration increases, nitrogen dioxide will be available for producing potentially undesirable nitrated byproducts. However, in the case of 2.6-dimethylnaphthalene, low solubility

of 6-formyl-2-naphthoic acid (29 grams/liter) and 2,6-naphthalenedicarboxylic acid (1 gram/liter) reduces the likelihood of undesirable nitration.

Modifications to Produce Oxidation Intermediates. A plot of composition *vs.* time for a batch oxidation of 2,6-dimethylnaphthalene in the presence of selenium is shown in Figure 4. It is obvious that stopping the

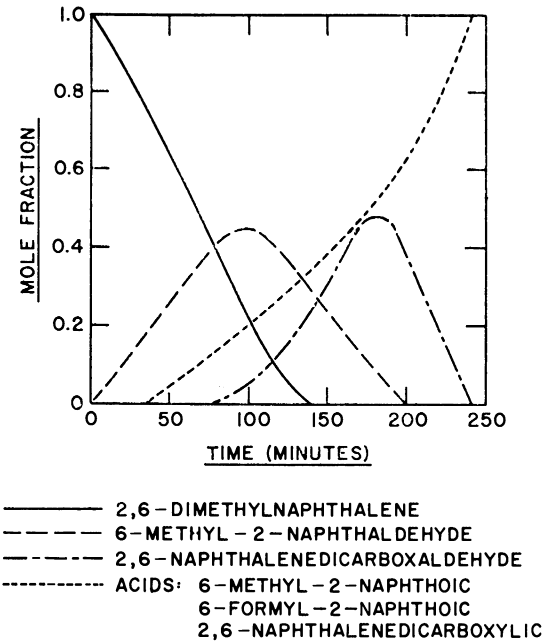
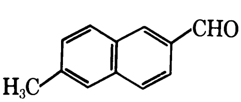
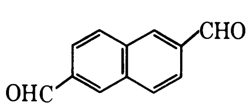


Figure 4. Composition vs. time for a batch oxidation of 2,6-dimethylnaphthalene at 195°C.

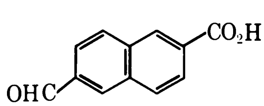
reaction at the appropriate time can produce significant yields of oxidation intermediates. Thus, appropriate modifications of reaction conditions can produce good yields of the following compounds, which have been isolated and unequivocally characterized:



M.P. = 119°–120°C.



M.P. = 176°–177°C.



M.P.–Dec.

Regeneration of Nitrogen Dioxide. An important process consideration in the overall use of this oxidation method is separating nitric oxide from the effluent gases, oxidizing it to nitrogen dioxide, and recovering the nitrogen dioxide for reuse. The oxidation of nitric oxide to nitrogen

dioxide using oxygen is known and proceeds according to the following stoichiometry:

$$2NO + O_2 \rightarrow 2NO_2$$

Enough information on this reaction is present in the literature (*1, 10, 14*) to indicate that regeneration of nitrogen dioxide can be accomplished without any anticipated serious problems. We estimate that 99.5% of the nitric oxide in the effluent gases can be converted to reusable nitrogen dioxide.

Safety Aspects. Realizing the potential toxicity of nitrogen dioxide, selenium, and selenium dioxide, precautions were taken to protect laboratory and pilot plant personnel directly involved with the oxidation. The concentration of nitrogen dioxide in the pilot plant atmosphere was monitored periodically to be sure that it remained within safe limits. Periodic physiological examinations of workmen revealed that selenium was being handled without incident. Therefore, the reactants can be and were handled safely by taking the ordinary precautions that should be taken with all potentially toxic chemicals.

Although many different solvents have been tried in this oxidation, trichlorobenzene emerged as the best overall solvent. Another item which concerned us was the formation of potentially hazardous nitrated byproducts, particularly from the trichlorobenzene solvent. Nitrated products are formed in this solvent during the course of hydrocarbon oxidations. In fact, we have actually isolated 3,4-dichloro-1-nitrobenzene. Therefore, the solvent is not completely inert during reaction conditions. A more detailed study of this nitration reaction was made by deliberately trying to nitrate the trichlorobenzene solvent by blowing nitrogen dioxide through the solvent in the absence of hydrocarbon or added selenium at reaction temperature. Dichloronitrobenzenes were detected, but only very small amounts of dinitrochlorobenzenes were observed. No trinitrated derivatives were detectable. Attempts to increase the quantity of dichloromononitro derivatives likewise were unsuccessful. Nitration apparently proceeds so slowly that no more than 1% of the trichlorobenzene solvent becomes nitrated even after recycling. Therefore, we conclude that nitration of the solvent does not present a serious safety hazard.

Application of Nitrogen Dioxide-Selenium Oxidations to Other Methylnaphthalenes

Laboratory data on the oxidation of a few representative methylnaphthalenes are summarized in Table II, where major products and unoptimized yields are listed.

Oxidation of 2-methylnaphthalene can be accomplished in the absence of selenium but at somewhat reduced yields. Oxidation of 1-methyl-

naphthalene to 1-naphthoic acid is more complicated and results in production of highly colored, nitrated by-products, which make the acid very difficult to purify. Therefore, oxidation of the 1-isomer is not practical in this system.

Table II. Oxidation of Methylnaphthalenes

Substance	*Selenium*	*Temperature, °C.*	*Major Product and Mole % Yield*
2-Methylnaphthalene	No	195	2-Naphthoic acid (75)
2-Methylnaphthalene	Yes	195	2-Naphthoic acid (92)
1-Methylnaphthalene	Yes	195	1-Naphthoic acid[a]
1,6-Dimethylnaphthalene	No	160–190	1,6-Naphthalenedicarboxylic acid (44)
1,6-Dimethylnaphthalene	Yes	185–195	1,6-Naphthalenedicarboxylic acid (75)
2,3-Dimethylnaphthalene	Yes	185–195	2,3-Naphthalenedicarboxylic anhydride (72)
Mixed dimethylnaphthalenes (1,3-, 1,6-, 1,7-, 2,6-, 2,7-)	Yes	195	Mixed Naphthalenedicarboxylic acids (86)

[a] Not determined owing to excessive by-product formation.

Oxidation of the dimethylnaphthalene isomers studied gives good yields of naphthalenedicarboxylic acids or anhydrides in the presence of selenium. Even for a mixture of dimethylnaphthalene isomers, good yields of the corresponding naphthalenedicarboxylic acids are obtained. However, when the methyl groups are adjacent, the anhydride is obtained. Since these anhydrides are more soluble than the corresponding dicarboxylic acids, the likelihood of nitration is increased and is actually observed in some cases. Generally speaking, however, oxidation of dimethylnaphthalenes proceeds readily using the nitrogen dioxide-selenium oxidation system.

Oxidation of Other Aromatic Substrates

A variety of organic aromatic materials can be oxidized to carboxylic acids or quinones (*11*), using nitrogen dioxide or a nitrogen dioxide-selenium system, as summarized in Table III.

Table III. Oxidation of Some Representative Aromatic Compounds

Substance	*Selenium*	*Temp., ° C.*	*Major Product and Mole % Yield*
2,6-Dimethyltetralin	Yes	195	2,6-Naphthalenedicarboxylic acid (65)
p-Xylene	No	140–195	Terephthalic acid (62)
o-Xylene	Yes, No	140–195	Phthalic anhydride (70–80)
1,2,4-Trimethylbenzene	No	165–195	Trimellitic acid (60)
1,2,4,5-Tetramethylbenzene	Yes	195	Pyromellitic hemianhydride (68)
p-*tert*-Butylbenzoic Acid	Yes	195	Terephthalic acid (25)
p-Toluic Acid	No	190–200	Terephthalic acid (60)
p-Nitrotoluene	No	195	*p*-Nitrobenzoic acid (62)
p-Chlorotoluene	No	190	*p*-Chlorobenzoic acid (77)
Anthracene	No	195	Anthraquinone (95)
Acenaphthene	No	210	Acenaphthenequinone (68)
Fluorene	No	190	Fluorenone (67)

2,6-Dimethyltetralin is dehydrogenated in the presence of selenium or selenium dioxide to give 2,6-dimethylnaphthalene which then proceeds to the dicarboxylic acid. Oxidation of polymethylbenzenes is also easily accomplished.

Presence of electron-withdrawing groups, such as chloro and nitro, do not prevent the conversion of methyl groups to the corresponding carboxylic acids, as exemplified by the oxidation of *p*-nitrotoluene and *p*-chlorotoluene.

Finally, oxidation of hydrocarbons such as anthracene, acenaphthene, and fluorene to the corresponding quinones in the absence of selenium indicates that the reaction can be adapted to produce other desirable products.

Conclusions

The preceding discussion has shown that oxidation with the nitrogen dioxide-selenium system is effective for converting methylnaphthalenes and alkylbenzenes to the corresponding carboxylic acids. Oxidation of methylbenzenes generally does not require the presence of selenium. Quinones have also been prepared from a few representative aromatics.

This oxidation method is versatile and has led to the production of some new and rather interesting aldehydic oxidation intermediates. The method has also been operated on a pilot plant scale to produce dimethyl 2,6-naphthalenedicarboxylate which we hope will lead to new and useful products.

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9

Cyanozonolysis of Olefins

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Hydroxy acids and amino acids have been synthesized by ozonolysis of olefins in aqueous emulsions of hydrogen cyanide (cyanozonolysis), followed by hydrolysis of the nitriles. For example, cyclo-octene gave 2,9-dihydroxysebacic acid, and cyclododecene gave 1,12-dihydroxydodecane-1,12-dicarboxylic acid. Indene, acenaphthylene, and 5-norbornene-2,3-dicarboxylic acid formed lactones. Cyanozonolysis in the presence of ammonia produced 1,12-diaminododecane-1,12-dicarboxylic acid from cyclododecene and 2-aminostearonitrile from 1-octadecene. This novel synthesis using ozone should be valuable in preparing many hydroxy and amino acids hitherto unknown or unavailable.

Cyclo-olefins have been ozonized in aqueous alkaline emulsions of hydrogen peroxide to give α,ω-dicarboxylic acids (*6*). In the presence of ammonia (amozonolysis), cyclo-olefins and ozone give widely differing products, depending on the olefin structure. Cyclopentadiene yields pyridine, indene, and isoquinoline; cyclohexene and cyclo-octene give imine polymers (*7*).

Ozonization of cyclo-olefins in emulsions of aqueous hydrogen cyanide—cyanozonolysis—now provides a novel synthesis of β,ψ-dihydroxy-α,ω-dicarboxylic acids containing two carbon atoms more than the original cyclo-olefin. In three cases, ammonia was used as an additional reagent, and amino acids resulted. Table I lists the products from cyanozonolysis of 16 cyclic and straight-chain olefins. The products were identified by elemental analysis, infrared, NMR, and mass spectroscopy, and mixture melting points.

Table I. Cyanozonolysis

Olefin	*Product*	*Yield, Mole %*
Cyclohexene	2,6-Diacetoxy suberonitrile	20
Cyclo-octene	1,8-Dihydroxy-1,8-dicyanooctane	57
	2,9-Dihydroxy sebacic acid	53
	2,9-Diacetoxy sebaconitrile	34
Cyclododecenc	1,12-Dihydroxydodecane-1,12-dicarboxylic acid	34
	1,12-Diacetoxy-1,12-dicyanododecane	43
	1,12-Diaminododecane-1,12-dicarboxylic acid	12
1,5-Cyclo-octadiene	1,8-Dicyano-1,8-diacetoxyoctene-4	27
1,5,9-Cyclododecatriene	1,12-Dicyano-1,12-diacetoxydodecadiene-4,8	20
α-Pinene	1,1-Dimethyl-2-acetyl cyclobutane-4-(2-acetoxy)propionitrile	34
Dicyclopentadiene	[i]	. . .
Indene	1-Oxoisochromane-3-carboxylic acid	32
Acenaphthylene	Naphthalide-3-carboxylic acid	34
5-Norbornene-2,3-dicarboxylic acid	Lactone of 1,2-dicarboxycyclopentane-3,5-diglycolic acid	7.5
1-Hexene	2-Acetoxy capronitrile	18
1-Octene	2-Hydroxycaprylic acid	10
1-Dodecene	2-Acetoxy-lauronitrile	41
	2-Acetamino-lauronitrile	22
1-Hexadecene	2-Hydroxypalmitonitrile	78
	2-Hydroxypalmitamide	100
	2-Aminopalmitonitrile hydrochloride	71
1-Octadecene	2-Hydroxystearonitrile	89
	2-Hydroxystearic acid	89
	2-Aminostearonitrile hydrochloride	27
	2-Aminostearic acid[e]	72
Stilbene	Mandelonitrile acetate	49
Methyl oleate	2-acetoxycapronitrile and methyl-9-cyano-9-acetoxypelargonate	43
		33

Saponification equivalent.
Mixture melting point with authentic 2-hydroxystearic acid, 90°-92°C.
Cl; calcd.—11.2; found—11.2
Cl; calcd.—12.3; found—11.9.
From 2-hydroxystearonitrile.
Molecular weight: calcd.—175; found (mass spectrum)—175.
Elemental analysis on undistilled material.
Molecular weight: calcd.—239; found (mass spectrum)—239.
See discussion.

of Olefins

M.P., °C.	Analysis							
	Calcd.			Neutral Equiv.	Found			Neutral Equiv.
	C	H	N		C	H	N	
b.p.$_{0.2}$ 161–3	57.2	6.3	11.1	...	57.2	6.7	10.9	...
...	61.2	8.2	14.3	...	60.7	8.0	14.7	
134	51.3	7.7	...	117	51.4	7.5	...	118
b.p.$_{0.5}$ 190–3	60.0	7.1	10.0	...	59.8	7.3	9.8	...
123–5	57.9	9.0	...	145	57.6	9.3	...	145
b.p.$_{0.2}$ 202–4	64.3	8.3	8.3	...	64.1	8.3	8.1	...
sl. dec. >440	58.3	9.7	9.7	...	58.0	9.8	9.6	...
b.p.$_{0.2}$ 170 dec.	60.4	6.5	10.1	...	60.8	6.8	9.8	...[g]
b.p.$_{0.3}$ 192–4	65.0	7.2	8.4	...	64.7	7.6	8.1	...
b.p.$_{1}$ 170–3	65.8	8.0	5.9	...	65.9	8.4	5.7	...
...	...	...	...	...	...	...	...	...
152–4	62.4	4.2	...	192	62.2	4.2	...	191
208–10	68.4	3.5	...	228	68.4	4.0	...	227
...	45.8	4.2	...	72[a]	45.4	4.4	...	71[a]
b.p.$_{0.2}$ 49	59.9	8.5	8.2	...	60.2	8.4	8.0	...
68	...	...	...	...	...	...	...	...
b.p.$_{0.5}$ 124–7	70.3	10.5	5.9	...[h]	70.6	10.8	6.0	...
b.p.$_{0.7}$ 60 187–90	70.6	10.9	11.8	...	70.3	11.1	11.6	...
33–4	...	...	...	...	...	...	...	...
148	...	...	...	...	...	...	...	...
94	66.6	11.4	9.7	...[d]	66.3	11.1	9.4	
45–7	76.3	13.1	4.9	...	76.0	12.9	4.7	...
91–2[b]	...	...	...	...	...	...	...	...
150	68.2	11.7	8.9	...[c]	68.6	11.9	8.5	...
224–5 dec.	72.2	12.4	4.7	...	71.9	12.2	4.5	...
b.p.$_{2.0}$ 120	...[f]	...	...	...	...	...	...	...
b.p.$_{0.2}$ 75–7	70.5	10.0	6.6	...	70.7	10.3	6.4	...
b.p.$_{1.2}$ 156–60	61.2	8.2	5.5	...	61.6	8.5	5.3	...

Experimental

Cyclo-octene and cyclododecene were obtained from Columbia Carbon Chemicals Co.; acenaphthylene from Rütgerswerke, A. G.; Brij. 30, used as an emulsifier, from the Atlas Co. All other materials were from Eastman Chemicals Co. The ozone was produced by a Welsbach T-23 ozonator in a concentration of 2.8–3.0 wt.% in oxygen.

A typical cyanozonolysis is described for cyclododecene. In a 1-liter Vibromix apparatus (Chemische Apparatus, Zürich) an emulsion of 37.5 grams (0.5 mole) of potassium cyanide (or 29.5 grams of sodium cyanide), 250 ml. water, 0.4 grams Brij. 30, and 37.3 grams (0.2 mole of 90%) cyclododecene was established by rapid mixing. At 0°C., 33.7 ml. (0.4 mole) concentrated hydrochloric acid was added, and then 14.4 grams (0.3 mole) ozone was passed in during 132 minutes. An additional 15 ml. concentrated hydrochloric acid was added to induce separation of the emulsion, which took one hour at 25°C. The semi-solid organic layer was separated from the aqueous phase and refluxed for three hours with 50 ml. ethanol, 20 ml. hydrochloric acid, and 200 ml. water. The mixture was evaporated to dryness on a steam bath, and the residue was dissolved in 5% aqueous sodium hydroxide. The alkaline solution was filtered, and the filtrate was acidified. The precipitated 1,12-dihydroxydodecane-1,12-dicarboxylic acid, 19.7 grams (34%), was crystallized from boiling water to give white crystals melting at 123°–5°C.

To prepare the diacetate of the dicyanohydrin, the semi-solid cyanohydrin from cyclododecene was heated with 150 ml. acetic anhydride and 1 ml. concentrated hydrochloric acid at 100°C. for 15 minutes (*15*). The cooled mixture was filtered and the filtrate distilled in vacuo, giving 29 grams (43%) light yellow 1,12-diacetoxy-1,12-dicyanododecane b.p.$_{0.2mm.}$ 202°–4°C., n_D^{20} 1.4545.

To isolate the hydroxy acids from 1-octene, cyclo-octene, indene, and 5-norbornene-2-,3-dicarboxylic acid, the cyanozonized emulsions were refluxed with hydrochloric acid for three hours and then evaporated to dryness on a steam bath. The residues were taken up in sodium hydroxide, filtered, acidified, and extracted thoroughly with ether. The ether extracts were dried and evaporated on the steam bath. Acenaphthylene was emulsified as a solution in ether prior to cyanozonolysis.

To compare the products from cyanozonolysis in a homogeneous system with those in an aqueous emulsion, 0.2 mole cyclo-octene and 0.6 mole hydrogen cyanide in 250 ml. ethanol containing 1 gram potassium hydroxide was ozonized at −10°C. with 0.3 mole ozone. Excess hydrogen cyanide was removed by blowing with air; the alcohol solution was refluxed with 50 ml. concentrated hydrochloric acid for two hours and evaporated. Ether was added, and the ether solution was extracted with base. Acidification of the alkaline extract gave 6.1 grams (13%) 2,9-dihydroxysebacic acid. The alkali-insoluble portion (21.1 grams) contained 13 components by gas chromatography. The major components were esters with appreciable amounts of aldehydes.

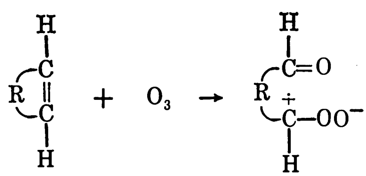
To obtain 1,12-diaminododecane-1,12-dicarboxylic acid, an emulsion of 49 grams (1 mole) sodium cyanide, 300 ml. water, 53.5 grams (1 mole) ammonium chloride, 20 ml. concentrated ammonium hydroxide, 0.5 grams of Brij. 30, and 37.3 grams (0.2 mole) cyclododecene was ozonized with 14.4 grams (0.3 mole) ozone at −5°C. This grand mixture was heated

at 80°C. for 30 minutes, and then was refluxed three hours with 300 ml. concentrated hydrochloric acid. The mixture was filtered and the cooled filtrate was brought to pH 8 by the addition of ammonium hydroxide. The solid was filtered, washed with water, and dried; it weighed 7.1 grams (12%). A portion was purified by solution in potassium hydroxide; the filtered solution was treated with excess hydrochloric acid and again filtered; the filtrate was brought to pH 8 with ammonium hydroxide to precipitate the amino acid.

The cyanozonolysis mixture from 0.2 mole of 1-octadecene was warmed with excess hydrochloric acid at 80°C. for 20 minutes. When it was cooled, 2-hydroxystearonitrile separated as a solid upper layer. This was crystallized twice from hexane to give 50.6 grams (89%) of white crystals melting at 45°–47°C. A portion, 2.83 grams (0.01 mole) was heated at 100°C. in a bomb with 5 ml. concentrated ammonium hydroxide and 2 grams ammonium carbonate. The product was refluxed three hours with excess hydrochloric acid, cooled, and filtered; the solid was refluxed two hours with 5 ml. ammonium hydroxide. The amino acid was collected on a filter, washed, dried, and crystallized from acetic acid with a little charcoal. It weighed 2.15 grams (72%) and melted at 224°–5°C. dec.; the literature melting point is 223°C. (*12*).

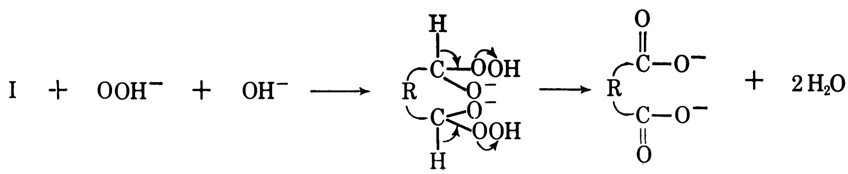
Discussion

In the ozonolysis of cyclo-olefins, the Criegee intermediate can be formulated as an aldehyde peroxy zwitterion (I):

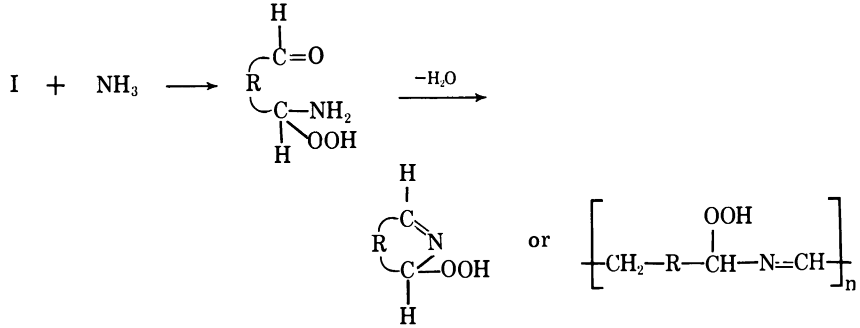


I

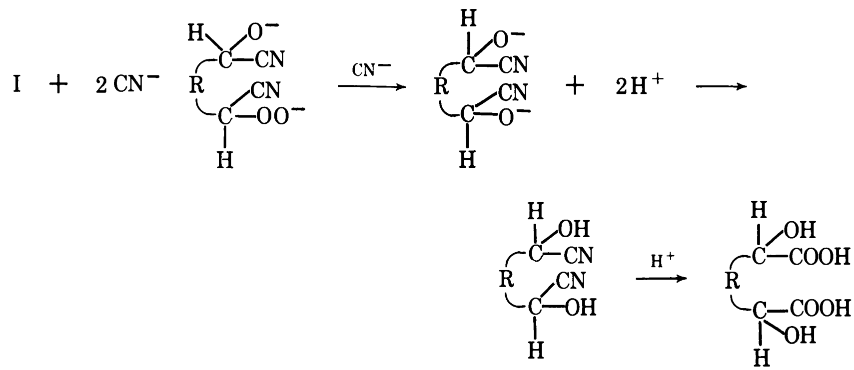
In aprotic solvents, the functional groups react rapidly to form polymeric ozonides or peroxides. In the presence of alkaline hydrogen peroxide, (I) gives α,ω-dicarboxylic acids in high yields by addition of hydroxy and hydroperoxy anions (*7*).



With ammonia, (I) reacts by intra- or intermolecular condensation:



In cyanozonolysis, cyanide ion adds to (I) to give the dicyanohydrin (II), which is hydrolyzed to the dicarboxylic acid (III):



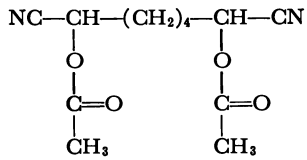
II III

Formation of the cyanohydrin II is catalyzed by cyanide ion; the rate-determining step is nucleophilic addition of cyanide ion to the carbonyl group (*9*). The reduction of hydroperoxide by hydrogen cyanide was tested by treating an emulsion of equimolar amounts of cumene hydroperoxide in toluene with aqueous hydrogen cyanide. At 0°C., 94.3% of the hydroperoxide was reduced in three minutes. This represents the least time necessary to establish the emulsion, withdraw aliquots, and titrate iodimetrically. The hydroperoxide may be reduced even more rapidly.

Cyanide ion reacts quickly with ozone in aqueous systems to give cyanate ion (*8, 14*). The yield of hydroxy acids by cyanozonolysis was increased appreciably by using a 50% molar excess of ozone over that of olefin; part of the ozone was destroyed by reaction with cyanide. When ozone was passed through an aqueous emulsion of hydrogen cyanide and pentane, only 15% came through unreacted. In addition, some ozone may have been lost by reaction with the aqueous alkaline emulsion (*6*).

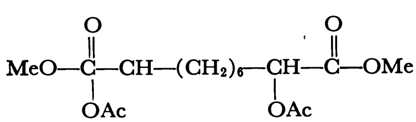
Although there have been some studies on the reaction of ozone with the carbon-nitrogen double bond (*4, 13*), there are none on its reaction with the carbon-nitrogen triple bond of nitriles. Ethylenic nitriles RR′—C=CR″—CN reacted with ozone to give products derived solely from attack at the carbon-carbon double bond (*3*). In our experiments, 80% of the ozone passed through an aqueous emulsion of acetonitrile was recovered unchanged. Evidently the nitrile structure is relatively unreactive towards ozone.

The dicyanohydrin from cyclohexene was isolated as the diacetate



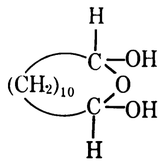
It had the correct elemental analysis. Its mass spectrum showed a small peak at 253 (parent plus one ion) but no parent peak. The 253 peak was the protonated parent arising from a bimolecular process, as shown by its sharp reduction in intensity when the residence time of the ions in the ion chamber was reduced. The rest of the mass spectrum was consistent with the structure, 2,7-diacetoxysuberonitrile.

Cyclo-octene gave the dicyanohydrin 1,8-dihydroxy–1,8-dicyano-octane, its diacetate, or 2,9-dihydroxysebacic acid depending on the work-up procedure. The melting point of our dihydroxysebacic acid was appreciably higher (134°C.) than those recorded in the literature (124°C., 125°–7°C., 130°C.). For comparison, dihydroxysebacic acid was synthesized from sebacic acid by brominating and solvolyzing the 2,9-dibromosebacic acid according to H. R. LeSueur (*10*). This acid melted at 132°–4°C.; the mixture melting point with the acid from cyanozonolysis was not depressed. For additional identification, the latter acid was esterified with methanol and acetylated. Its mass spectrum revealed no peak at mass 346, but this is common with large oxygenated compounds. There was a peak at 347 that was pressure-dependent. This clearly arose by a bimolecular process, and furnished strong support for 346 as the molecular weight. The other prominent peaks and metastable peaks fit together into a reasonable decomposition scheme for the structure

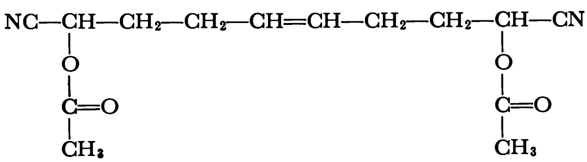


Cyanozonolysis of cyclo-octene, followed by acetylation, gave 2,9-diacetoxysebaconitrile. This could be distilled in only small quantities since continued heating caused considerable decomposition.

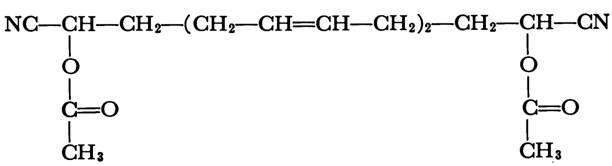
Cyclododecene gave, in addition to 1,12-dihydroxydodecane-1,12-dicarboxylic acid, a 10% yield of a white solid melting at 85°–87°C. of empirical formula $C_{12}H_{24}O_3$. It was not a peroxide or ozonide; its infrared spectrum contained strong bands for OH and C—O stretch, but only a weak C=O. Both infrared and NMR spectra were consistent with the structure



Polyolefins could be cyanozonized to unsaturated cyanohydrins, isolated as the acetates. 1,5-Cyclo-octadiene gave 1,8-dicyano-1,8-diacetoxyoctene-4;

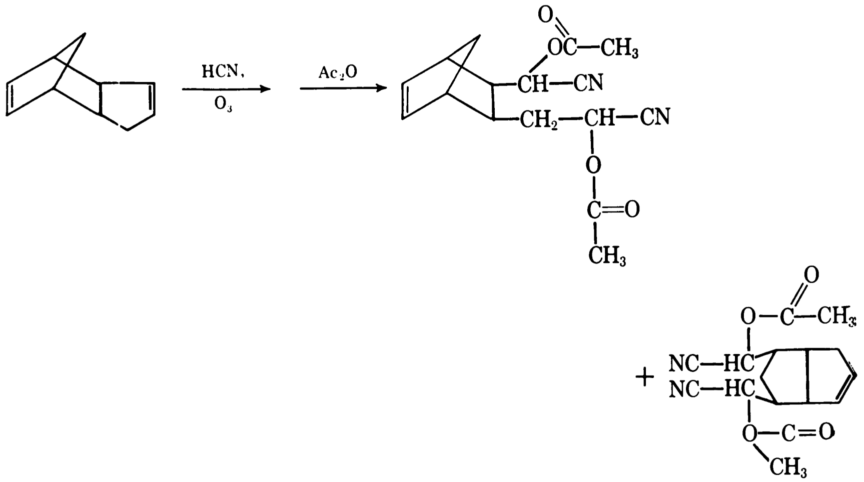


The crude material was obtained fairly purely, but on attempted distillation it decomposed extensively. 1,5,9-Cyclododecatriene gave 1,12-dicyano-1,12-diacetoxydodecadiene

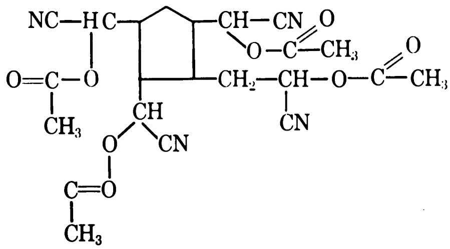


that proved more stable to distillation. The trans olefin band was evident in the infrared at 1038 $cm.^{-1}$ The greater thermal stability of the trans olefinic dicyanohydrin compared to the cis compound from cyclo-octadiene suggests the functional groups of the latter react intramolecularly at elevated temperatures. The NMR and mass spectra were consistent with the structures shown, but the exact locations of the double bonds were not proved.

Dicyclopentadiene was cyanozonized both partially and completely. With one mole of ozone, it gave probably a mixture of the two cyanohydrins.

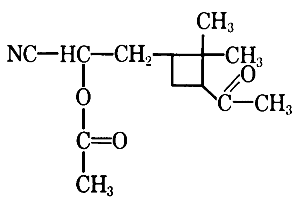


On complete ozonization with an excess over two moles of ozone, it yielded the tetracyanohydrin tetra-acetate



The products could not be crystallized or distilled without extensive decomposition. Elemental analyses, therefore, were on impure materials and were not in the acceptable range, although indicating 85–90% purity. The mass spectra showed the presence of ions of correct molecular weight for the expected cyanohydrin acetates.

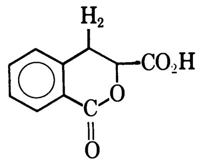
α-Pinene was cyanozonized at 0°C. Distillation of the acetylated product gave the monocyanohydrin, 1,1-dimethyl-2-acetylcyclobutane-4-(2-acetoxy)propionitrile.



This had the correct elemental analysis and mass spectrum. Ozonizing at 20°C. and recovering the product without distillation gave a mixture of

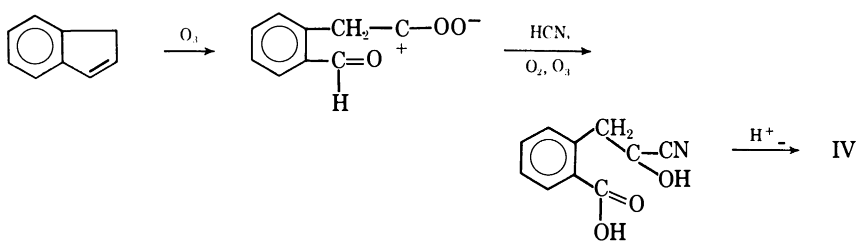
mono and dicyanohydrin acetates. 1-Methylcyclohexene gave similar results: the dicyanohydrin diacetate decomposed vigorously on attempted distillation. The undistilled product had an elemental analysis indicating a mixture of ketone cyanohydrin acetate and dicyanohydrin diacetate.

The product from indene was assigned the structure of the lactone (IV) 1-oxoisochroman-3-carboxylic acid:



IV

This was done on the basis of its elemental analysis, neutral equivalent, and mass and infrared spectra of its methyl ester. The acid OH absorbed at 3300–2500 cm.$^{-1}$; there were two types of carbonyl, at 1750 and 1725 cm.$^{-1}$ Treatment with alkali shifted the 1725 band to the carboxylate region, leaving the 1750 cm.$^{-1}$ band. This compound, melting at 153.5°C., had been previously made in a four-step synthesis from 1,2-naphthoquinone (*1*). Its formation appears to involve oxidation of the aldehyde end and reductive cyanohydrin formation from the hydroperoxide end followed by ring closure on hydrolysis with acid:

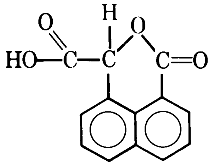


Since the yield was less than 50%, the 2-carboxyl group of the intermediate might have formed by a Cannizarro reaction induced by the alkaline medium rather than by oxidation.

To investigate this point, stilbene was cyanozonized. Mandelonitrile, isolated as the acetate, was formed in 49% yield. Some stilbene was recovered; the yield of benzoic acid was only 3%. This left undetermined the mode of formation of the oxoisochroman ring from indene but indicated that oxidation (or disproportionation) of the aldehyde group did not occur to an appreciable extent under cyanozonolysis conditions, unless ring formation was possible.

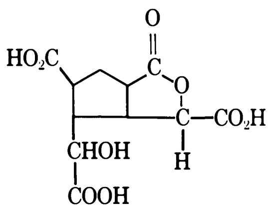
The acid from acenaphthylene was esterified and purified by gas chromatography. Its mass spectrum showed the parent ion at 242: three strong peaks arose in a single reaction sequence (as shown by metastable

peaks) at 183, 155, and 127, by loss of $CH_3{-}O\underset{\overset{\|}{O}}{C}$, CO, and CO, respectively. This behavior exactly paralleled that of IV under electron impact; the original acid therefore was naphthalide-3-carboxylic acid:



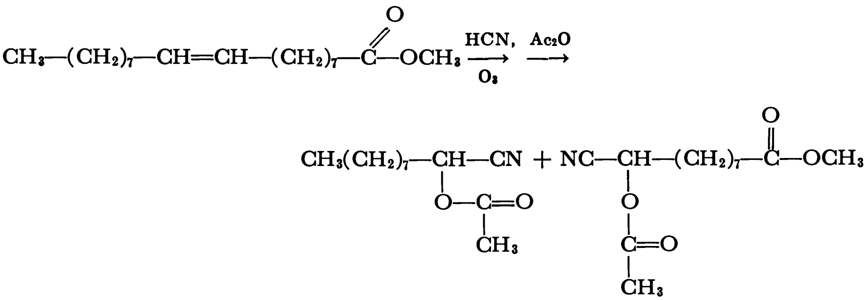
It had previously been prepared in four steps from perinaphthindane-1,3-dione (*5*).

Cyanozonolysis of 5-norbornene-2,3-dicarboxylic acid gave a viscous syrup that refused to crystallize. The neutral and saponification equivalents showed the presence of an ester group, and the probable structure of the product is:



1-Octene and 1-octadecene gave 2-hydroxycaprylic and 2-hydroxystearic acids, respectively. The large difference in the yields—10% *vs.* 89%—is probably caused by the much greater ease of isolating and purifying the cyanohydrin from 1-octadecene. This was generally the case: the lower yields usually reflected greater difficulty in isolating highly water soluble products. Our 2-hydroxystearonitrile melted at 45°–47°C.; the literature gives 61.5°–62.5°C. (*11*). The product from cyanozonolysis went quantitatively to 2-hydroxystearic acid on hydrolysis, and to 2-hydroxystearamide on partial hydrolysis (*11*). It had the correct elemental analysis and clearly showed the hydroxyl absorption in the infrared. On this basis we believed that our melting point was correct. In common with other 2-hydroxy nitriles (*2*), our compound showed no CN absorption in the infrared at 2260 cm.$^{-1}$

Methyl oleate was cyanozonized in ether, rather than water, to avoid thick emulsions and foaming. Usually, aqueous emulsions were preferred since more by-products were formed in ether solution. These not only lowered yields but decomposed extensively on attempted distillation. The acetylated mixture gave, on distillation, 2-acetoxycapronitrile and 2-acetoxysebacic half nitrile half methyl ester.



Cyanozonolysis of cyclododecene in the presence of ammonia gave, after workup, a product that was soluble in both acids and bases, did not melt at 440°C., and had the correct elemental analysis and infrared spectrum for 1,12-diaminododecane-1,12,dicarboxylic acid. Its mineral oil mull with a very low mineral oil content showed $(CH_2)_n$ absorbance at 725 cm.$^{-1}$ where $n = > 6$; ionized carbonyl bands of an amino acid at 1587 and 1410 cm.$^{-1}$; and NH_3^+ bands of an amino acid zwitterion at 3078, 1613, and 1515 cm.$^{-1}$

Similar treatment of 1-octadecene gave the hydrochloride of 2-aminostearonitrile as a solid of unsharp melting point, soluble in water to form a foaming solution. Its infrared spectrum showed bands at 3300–2500 cm.$^{-1}$ for NH_3^+, but no absorption at 2260 cm.$^{-1}$ for CN. A good yield of 2-aminostearic acid resulted from the reaction of 2-hydroxystearonitrile (by cyanozonolysis of 1-octadecene) with ammonium hydroxide at 100°C., followed by hydrolysis.

Ozonolysis of 1-dodecene in the presence of ammonia and hydrogen cyanide, followed by acetylation and distillation, gave 2-acetaminolauronitrile. As was true of many of the compounds of this work, its mass spectrum showed both the parent ion and the parent plus one ion.

Cyanozonolysis of olefins should be a valuable new method for the synthesis of many hydroxy and amino acids that hitherto have been unknown or unavailable. Variations in reaction and workup procedures allow the isolation of intermediates and increase the versatility of the process. Thus, cyanohydrins, α-acetoxynitriles, α-hydroxyamides, α-aminonitriles, and α-acetaminonitriles may be readily obtained from the original cyanozonolysis products.

Acknowledgment

The author is greatly indebted to these members of the Analytical Division of the American Oil Co.: A. G. Nerheim for stimulating and informative discussions of the infrared spectra; S. Meyerson for his interpretation of the mass spectra; and to G. Powers for esterification gas chromatography.

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10

Oxidation of Hydrocarbons in Basic Solution

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The oxidation of carbanions is reviewed, and new experimental details are provided. Electron spin resonance techniques demonstrate the presence of paramagnetic intermediates, and in some instances the oxidative mechanism is specified. All results are consistent with carbanion–radical-anion chain mechanisms. However, the details of the chain process vary greatly with the structure of the carbanion being oxidized. The rate of oxidation of certain hydrocarbons in basic solution can be used to measure the rate of ionization of the parent hydrocarbon. Other carbanions are formed readily but oxidized slowly. Certain carbanion oxidations are further complicated by autocatalysis from a reaction intermediate, while many nitro-substituted carbanions undergo spontaneous electron transfer forming paramagnetic intermediates that can be observed in the absence of oxygen.

A wide variety of carbanions and nitranions react with molecular oxygen to yield either oxygenated or dehydrogenated products. The oxidation of hydrocarbons and their derivatives in basic solution can be a highly selective process and one that shows selectivity differing from conventional oil-phase autoxidations. Thus, in *tert*-butyl alcohol containing potassium *tert*-butoxide the oxidation of a mixture of fluorene and triphenylmethane quantitatively converts the fluorene to fluorenone without any attack on triphenylmethane, the least acidic hydrocarbon. Similarly, in dimethyl sulfoxide (80%)–*tert*-butyl alcohol (20%) only triphenylmethane is oxidized in a mixture of triphenylmethane and cumene.

The generalization has been made that "oxidation processes which do not involve the direct addition of oxygen probably take place in steps of single electron transfer" (39). This almost certainly is the case when the dehydrogenation is intramolecular in nature (53, 70, 87). Dehydrogenations of this type are recognized when

$$H{-}X{-}Y{-}H \overset{B^-}{\rightleftharpoons} H{-}X{-}Y^- \overset{B^-}{\rightleftharpoons} {}^-X{-}Y^-$$

$${}^-X{-}Y^- + O_2 \rightarrow \cdot X{-}Y^- + O_2\cdot^-$$

$${}^-X{-}Y^- + O_2\cdot^- \rightarrow \cdot X{-}Y^- + O_2^{-2}$$

$${}^-X{-}Y^- + X = Y \rightleftharpoons 2 \cdot X{-}Y^-$$

$$\cdot X{-}Y^- + O_2 \text{ (or } O_2\cdot^-) \rightarrow X{=}Y + O_2\cdot^- \text{ (or } O_2^{-2})$$

H—X—Y—H is an α-hydroxyketone (*13, 40, 88, 89, 90, 91, 92, 93, 95*), an *o*- or *p*-hydroquinone (*41, 42, 50*), a 1,4-diketone (*1, 2, 14, 15, 20*), 2,4-cycloheptadienone (*82*), 9,9′-bifluorene (*83*), *p,p*′-dinitrobibenzyl (*28, 29*), hydrazobenzene (*16, 75*), diarylcarbinols (*26, 27, 48, 49*), or hydroxylamines (*44*), or where ⁻X—Y⁻ is the dialkali metal adduct of stilbene (*71*), azobenzene (*71*), tetraphenylethylene (*38*), anthracene (*38*), and fulvalene (*23, 54, 74*).

At present we would like to consider the mechanisms involved in the reaction of molecular oxygen with carbanions to form oxygenated products. It appears to be well established that the initial reaction product is the salt of a hydroperoxide which can either be stable (*5, 8, 31, 32, 35, 38, 56, 76, 86*), or which can undergo base-catalyzed decomposition (*5, 35, 46, 61*) sometimes with carbon—carbon bond scission (*5, 24, 46, 61*).

$$R_2CHOOH + B^- \rightarrow R_2CO + HB + OH^-$$

$$R_2CHOOH + R^- \rightarrow R_2CHO^- + ROH$$

$$R_3COOH + R^- \rightarrow R_3CO\cdot + OH^- + R\cdot$$

$$RCO\overset{\overset{\displaystyle OOH}{|}}{C}R_2 + OH^- \rightarrow RCO_2^- + R_2CO + H_2O$$

$$R_2\underset{\underset{\displaystyle OOH}{|}}{C}CO_2H + OH^- \rightarrow R_2CO + CO_2 + OH^-$$

The alcohols, ketones, and acids often observed as oxidation products thus arise as primary or secondary reaction products formed from the initial hydroperoxide (*60*).

The mechanism of the initial formation of the hydroperoxide in the oxidation of carbanions is under dispute. Fairly conclusive evidence has been presented that the autoxidation of certain nitroalkanes in basic solution involves a free-radical chain process (*61*).

$$R{:}^- + ROO\cdot \rightarrow ROO{:}^- + R\cdot$$

$$R\cdot + O_2 \rightarrow ROO\cdot$$

However, little enthusiasm has been shown by other workers for this

two-step process even though there is evidence for a facile initiation process. For example, in the presence of deficient quantities of oxygen the perinaphthenide anion is converted to the 1-phenalenyl radical (*84*).

In the oxidation of Grignard reagents, Walling and Buckler (*86*) found no evidence for a radical chain process, although it must be admitted that for organometallic reagents the presence of the metal cation may have a profound effect on the details of the reaction. Evidence against the chain process and in favor of a one-step reaction—$R:^- + O_2 \rightarrow ROO:^-$—has been presented by Sprinzak in a study of the oxidation of fluorene (*76*) and by Gersmann, Nieuwenhuis, and Bickel in a study of the oxidation of unsaturated esters (*32*).

The one-step mechanism shown above bears the dubious distinction of being one of the few (if not the only) organic process which involves a change in multiplicity concurrent with bond formation. It would appear that the probability of a change in electronic spin at the same time that a bond is being formed or broken would be prohibitive. At best, the process would require an intermediate, for example, (a) singlet oxygen, (b) a triplet carbanion, (c) a radical-pair (*32*) ($R\cdot \uparrow\uparrow \cdot OO:^- \rightarrow R\cdot \uparrow\downarrow \cdot OO:^-$), or (d) an intermediate triplet state for $ROO:^-$.

We will consider in some detail the oxidation of fluorene (R_2CH_2) to fluorenone (R_2CO) in basic solution (*76*) and show conclusively that

$$R_2CH_2 + B^- \rightarrow R_2CO + H_2O$$

this oxidation proceeds by a carbanion-radical chain mechanism. These results will then be extended to other polyarylmethanes, substituted toluenes, benzhydrols, polyarylethanes, nitroalkanes, and ketones.

Oxidation of Fluorene in Basic Solution

Solvent Effects on Rate of Oxidation. Fluorene is oxidized by molecular oxygen in the presence of potassium *tert*-butoxide in *tert*-butyl alcohol solution or more readily in mixtures of *tert*-butyl alcohol and benzene, dioxane, morpholine, piperidine, pyridine, hexamethylphosphoramide, dimethylformamide, or dimethyl sulfoxide (DMSO). As little as 10 volume % of DMSO added to *tert*-butyl alcohol enhanced the rate of oxidation by 19-fold. Some typical results are summarized in Figure 1 and Table I.

The solvent effects upon the oxidation rate of fluorene are quite suggestive of a process involving ionization to yield the fluorenide anion which is then consumed by reaction with molecular oxygen. The rate of oxidation increases with fluorene and base concentration, but it is by no means limited by the rate of ionization. The rate depends upon the concentration (partial pressure) of oxygen, and the oxidation can be catalyzed by a wide variety of electron-accepting agents.

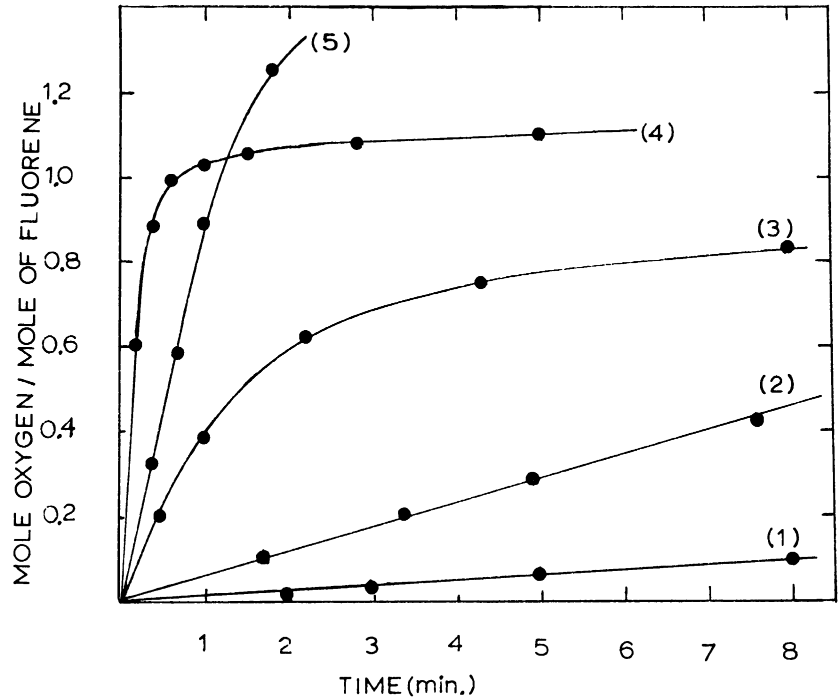


Figure 1. Autoxidation of fluorene (0.1M) in presence of 0.2M potassium tert-*butoxide; (1)* tert-*butyl alcohol; (2) benzene (80%)–*tert-*butyl alcohol (20%); (3) dioxane (80%)–*tert-*butyl alcohol (20%); (4) dimethyl sulfoxide (80%)–*tert-*butyl alcohol (20%); (5) piperidine (80%)–*tert-*butyl alcohol (20%)*

Table I. Initial Rates of Oxidation of Fluorene in Presence of Potassium *tert*-Butoxide[a]

Solvent	*Initial Rate[b]*	*Relative Rate*
tert-BuOH	0.02	1.0
Benzene(80)–*tert*-BuOH(20)	0.05	2.5
Dioxane(80)–*tert*-BuOH(20)	0.38	19
Morpholine(80)–*tert*-BuOH(20)	0.81	41
Piperidine(80)–*tert*-BuOH(20)	0.90	45
Pyridine(80)–*tert*-BuOH(20)	1.8	90
Hexamethylphosphoramide(80)–*tert*-BuOH(20)	3.2[c]	160[c]
Dimethylformamide(80)–*tert*-BuOH(20)	4.1[c]	205[c]
DMSO(80)–*tert*-BuOH(20)	4.4[c]	220[c]
DMSO(10)–*tert*-BuOH(90)	0.38	19
DMSO(80)–*tert*-BuOH(20)[d]	1.4	70
DMSO[e]	1.0	50
DMSO–CH_3OH[f]	1.4	70

[a] 25 ml. of a solution initially 0.12*M* in fluorene and 0.19*M* in potassium *tert*-butoxide at 25° ± 2° C.
[b] Moles oxygen/mole fluorene per min.
[c] Probably diffusion-controlled rate.
[d] Saturated solution of lithium *tert*-butoxide.
[e] Saturated solution of potassium hydroxide.
[f] Solvent consisted of 15 ml. DMSO and 10 ml. of a 40% solution of benzyltrimethylammonium methoxide in methanol.

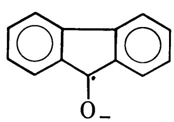
Fluorenone was obtained as the major oxidation product in all solvent mixtures except for certain solutions containing DMSO. Solutions containing 80% or more by volume of DMSO gave as the major reaction product the DMSO-fluorenone adduct, 9-hydroxy-9-(methylsulfinylmethyl)fluorene in the presence of potassium *tert*-butoxide. Some typical yields are given in Table II.

Table II. Oxidation Products of Fluorene in DMSO–*tert*-BuOH Solution

			Product, %	
Fluorene (Mmoles)	*tert-BuOK (Mmoles)*	*DMSO % by Vol.*[a]	*Fluorenone*	*9-Hydroxy-9-(Methylsulfinylmethyl)-fluorene*
2.91	6.0	0	91	
2.97	6.0	80	0	78.0
3.08	3.0	80	0	74.0
2.92	6.1	10	88	8.6
3.15	[b]	100	70	12.0

[a] *tert*-Butyl alcohol cosolvent.
[b] Saturated solution of potassium hydroxide.

During oxidations in DMSO solutions the red color of the fluorenide anion was replaced by a purple color which became green upon completion of the oxidations. The green color was also observed when fluorenone was dissolved in DMSO(80%)–*tert*-butyl alcohol (20%) in the presence of potassium *tert*-butoxide. Attempts were made to detect paramagnetic intermediates in the autoxidations by electron spin resonance spectroscopy (ESR). In *tert*-butyl alcohol paramagnetic species could not be observed during oxidation or after an oxidation had been halted before the fluorene had been completely consumed. However, in pyridine (80%)–*tert*-BuOH(20%) or DMSO(80%)–*tert*-BuOH(20%) solutions a strong ESR signal could be detected during oxidation or after an interrupted oxidation. The spectrum was recognized as that of fluorenyl ketyl radical-anion.



The spectrum of this ketyl has been reported in DMSO–*tert*-butyl alcohol solutions (*62, 63*) as well as in dimethylformamide solution (*21*). The formation of fluorenyl ketyl was not surprising. Futhermore, it is not pertinent to the oxidation mechanism since it can also be formed in these solvents in the presence of potassium *tert*-butoxide by (a) oxidation of 9-fluorenol, (b) electron transfer between the alcohol and the ketone (*62*), or (c) electron transfer between fluorenyl anion or other anions and the ketone (*63*). Since the oxidation of 9-fluorenol in *tert*-butyl alcohol–potassium *tert*-butoxide does yield detectable amounts of the ketyl, it

must follow that 9-fluorenol is not an intermediate that reaches an appreciable concentration in the oxidation of fluorene in *tert*-butyl alcohol.

Catalysis of Fluorene Oxidation. No significant effect on the rate of oxidation of fluorene in *tert*-butyl alcohol–potassium *tert*-butoxide was observed when small amounts of ferric chloride, arsenic trioxide (*64*), or fluorenone were added. Ferric chloride and arsenic trioxide which have a pronounced effect on the rate of oxidation of 2-nitropropane in aqueous base and to a lesser extent in alcoholic solution (*61*), also had no effect upon rates of oxidation of fluorene in DMSO(80%)–*tert*-BuOH(20%) in the presence of deficient concentrations of potassium *tert*-butoxide.

In *tert*-butyl alcohol solution a number of nitroaromatics significantly accelerated the rate of oxidation of fluorene in the presence of potassium *tert*-butoxide (Figure 2, Table III).

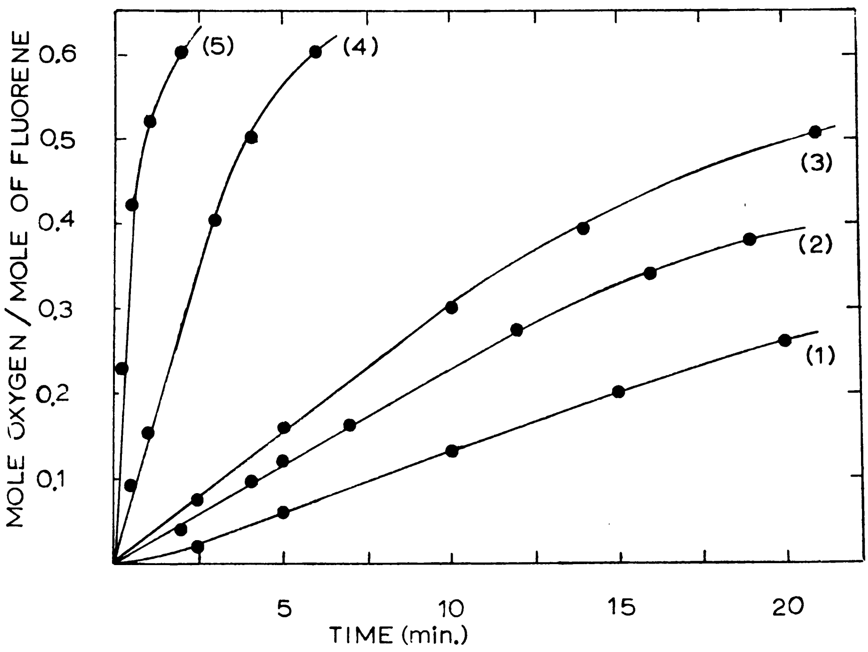


Figure 2. Catalyzed autoxidation of 0.10M fluorene in tert-butyl alcohol containing 0.2M potassium tert-butoxide; (1) uncatalyzed; (2) 0.005M m-nitroltoluene; (3) 0.005M nitrobenzene; (4) 0.005M p-chloronitrobenzene; (5) 0.005M p-cyanonitrobenzene

In a separate set of experiments electron transfer from the fluorenide anion to nitrobenzenes was monitored by ESR spectroscopy (*63*). Solutions of appropriate concentrations of the anion and nitrobenzene were mixed and allowed to flow immediately into the ESR cell. In Figure 3 the observed potentiometer deflections are plotted as a function of time

Table III. Initial Rates of Catalyzed Oxidations of Fluorene in *tert*-Butyl Alcohol[a]

Catalyst[b]	*Initial Rates* *Autoxidation*[c]	*Electron Transfer*[d]
None	0.015	0.00
6-Nitroquinoline	0.016	...
m-Nitroaniline	0.016	0.02
m-Nitrotoluene	0.027	0.055
1,3,5-Trinitrobenzene[e]	0.030	...
Nitrobenzene	0.036	0.10
Nitrobenzene[f]	0.075[g]	...
Nitrobenzene[h]	1.6[i]	...
m-Methoxynitrobenzene	0.038	0.135
Pentachloronitrobenzene	0.040	...
p-Dimethylaminonitrobenzene	0.12	...
p-Chloronitrobenzene	0.17	0.30
p-Bromonitrobenzene	0.21	...
m-Dinitrobenzene	0.30	...
m-Cyanonitrobenzene	0.57	...
p-Dinitrobenzene	0.7	...
p-Cyanonitrobenzene	0.7	3
4-Nitropyridine *N*-oxide	1.0	...
m-Trifluoromethylnitrobenzene		0.60

[a] 0.10*M* fluorene, 0.20*M* potassium *tert*-butoxide, 25° ± 2° C.
[b] 4.8 mmoles/liter.
[c] Moles oxygen/mole fluorene per min.
[d] Mmoles of nitroaromatic radical-anion/liter-min.
[e] 3 mmoles/liter
[f] 9.8 mmoles/liter
[g] 0.12*M* fluorene, 0.24*M* potassium *tert*-butoxide.
[h] 0.4*M*.
[i] 0.15*M* fluorene, 0.4*M* potassium *tert*-butoxide.

for overmodulated ESR signals observed (after flow had been stopped) at a magnetic field setting to give maximum absorption. The resolved spectra were compatible with the nitrobenzene radical-anions. For example, the spectrum observed with nitrobenzene as the acceptor in *tert*-butyl alcohol is given in Figure 4. This spectrum is consistent with the nitrobenzene radical-anion with $a_N = 12.74$, $a_{o-H} = a_{p-H} = 3.46$, and $a_{m-H} = 1.15$ gauss.

The initial rates of electron transfer from the fluorenide anion to the nitroaromatics is given in column 3 of Table III. Although the absolute rates may be in error by ± 30%, the relative rates are believed to be quite accurate. *p*-Cyanonitrobenzene, *m*-cyanonitrobenzene, and *m*-dinitrobenzene gave very rapid electron transfer reactions with the fluorenide anion, but the resulting radical-anions decayed fairly rapidly. The typical behavior of *p*-cyanonitrobenzene is shown in Figure 5. The maximum concentration of the *p*-cyanonitrobenzene radical-anion was achieved about 45 seconds after mixing the solutions, with two-thirds of this maximum concentration being formed in less than 10 seconds.

The effect of *m*- and *p*-substituents on the nitrobenzene-catalyzed autoxidation of the fluorenide anion and the rate of electron transfer from the anion are compared in Figure 6 with the σ-constants of the substituents. For the catalyzed oxidations the ordinate of Figure 6 is log

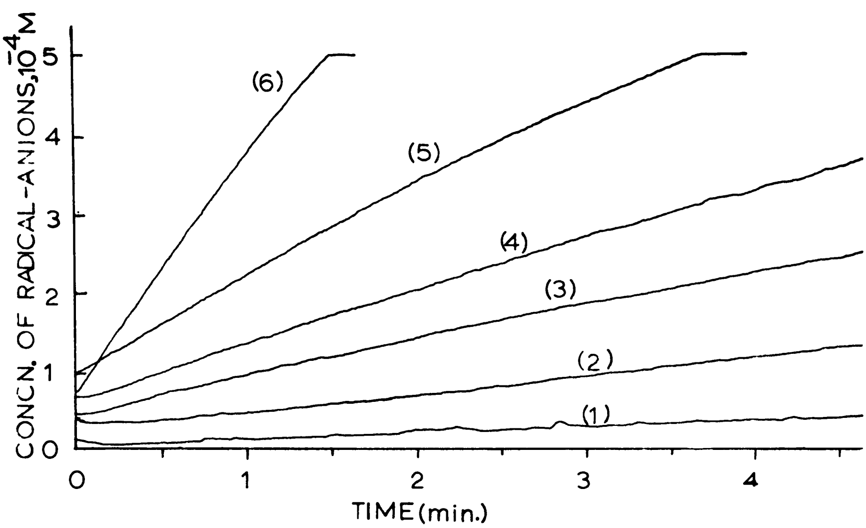


Figure 3. Nitroaromatic radical-anion formation in tert-*butyl alcohol at 25°C. from the reaction of 0.10*M *fluorene, 0.20*M *potassium* tert-*butoxide and 4.8 mmoles/liter of (1)* m-*nitroaniline, (2)* m-*nitrotoluene, (3) nitrobenzene, (4)* m-*nitroanisole, (5)* p-*chloronitrobenzene, (6)* m-*nitrobenzotrifluoride. Radical-anion concentrations at zero time reflect reaction occurring during the filling of the ESR cell. Signal deflection at constant field obtained by overmodulation of ~9,500 Mc./sec. spectrometer with 100 Kc./sec. field modulation*

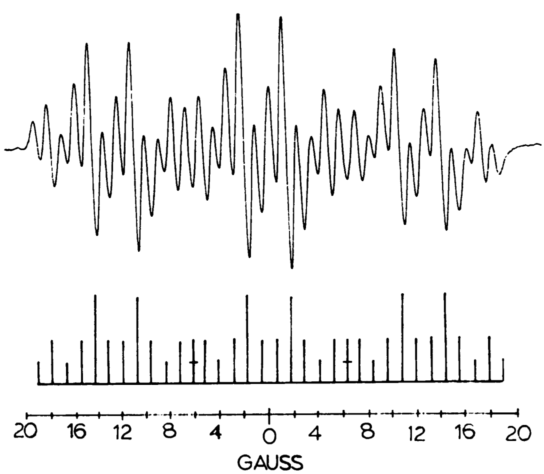


*Figure 4. Spectrum of nitrobenzene radical-anion prepared by the reaction of fluorene (0.1*M*), potassium* tert-*butoxide (0.2*M*) and nitrobenzene (4.8 mmoles/liter) in* tert-*butyl alcohol at 25°C.* $\pm 2°$

(initial rate of oxidation catalyzed by substituted nitrobenzenes/initial rate of oxidation catalyzed by nitrobenzene), while for the electron transfer experiments the ordinate is log (rate with substituted nitrobenzene/rate with nitrobenzene).

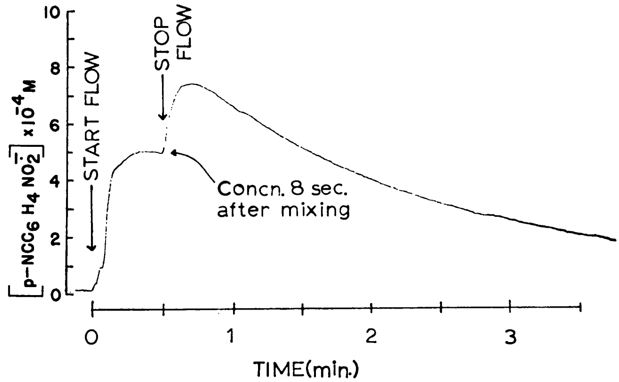


*Figure 5. Magnitude of ESR signal at constant field as a function of time for solutions 0.1*M *in fluorene, 0.2*M *in potassium* tert-*butoxide, and 4.8 × 10^{-3}*M *in* p-*cyanonitrobenzene*

It is obvious from Figure 6 that both reactions have similar substituent effects. It follows that in the catalyzed oxidations the observed relative rates are determined mainly by the catalytic step, and this step is one of electron transfer.

$$R_2CH:^- + ArNO_2 \rightarrow R_2CH\cdot + ArNO_2\cdot^-$$

$$R_2CH\cdot + O_2 \rightarrow R_2CHOO\cdot$$

$$R_2CHOO\cdot + R_2CH:^- \rightarrow R_2CH\cdot + R_2CHOOH \xrightarrow{B^-} R_2CO + H_2O$$

$$ArNO_2\cdot^- + O_2 \rightarrow ArNO_2 + O_2\cdot^-$$

The effect of the structure of nitroaromatic catalyst on the oxidation rate can also be correlated with the half-wave one-electron reduction potentials observed for the nitroaromatics in acetonitrile solution (*51*).

The product of the oxidation of fluorenide anion catalyzed by nitroaromatics was again fluorenone with 1 mole of oxygen absorbed per mole of fluorene. In the presence of a large excess of nitrobenzene (e.g. 300%, *see* Table III), a minimum yield of 64% of fluorenone was isolated.

The kinetic chain length of the autoxidation of fluorenide ion can be estimated from Table III. The initial rate of oxidation of 0.10*M* fluorene (0.2*M* potassium *tert*-butoxide in *tert*-butyl alcohol) was 0.0015 moles oxygen/liter-min., while in the presence of 0.0048*M* nitrobenzene the rate

was increased to 0.0036 moles oxygen/liter-min. ($\Delta R_{O_2} = 0.0021$). The rate of initiation found for the reaction of 0.10*M* fluorene in 0.2*M* potassium *tert*-butoxide with 0.0048*M* nitrobenzene was 0.0001 moles of electron transfer product/liter-min. Hence, the formation of one fluorenyl radical leads to the consumption of approximately 21 molecules of fluorene —i.e., a kinetic chain length of about 21.

Mechanism of Oxidation of Fluorene in Basic Solution. The results presented are consistent with the following oxidation mechanism for fluorene (R_2CH_2) in basic solution.

$$R_2CH_2 + B^- \rightleftharpoons R_2CH{:}^- + HB \quad (1)$$

$$R_2CH{:}^- + O_2 \rightarrow R_2CH\cdot + O_2\cdot^- \quad (2)$$

$$R_2CH{:}^- + O_2\cdot \text{ [or } HOO\cdot) \rightarrow R_2CH\cdot + O_2^{-2} \quad (3)$$

$$R_2CH{:}^- + A \text{ (catalyst)} \rightarrow R_2CH\cdot + A\cdot^- \quad (4)$$

$$A\cdot^- + O_2 \rightarrow A + O_2\cdot^- \quad (4')$$

$$R_2CH\cdot + O_2 \rightarrow R_2CHOO\cdot \quad (5)$$

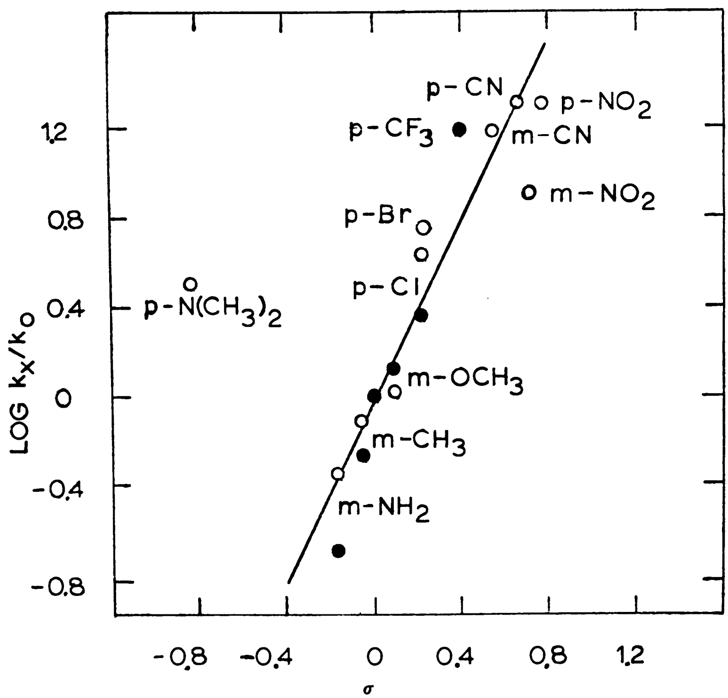


Figure 6. Hammett correlation between substituent constants, the rate of electron transfer from the fluorenide anion to substituted nitrobenzenes (○), and the catalyzed oxidation observed with substituted nitrobenzenes (●). For all experiments the ordinate is log (initial rate with substituted nitrobenzenes/initial rate with nitrobenzene)

$$R_2CH\cdot + O_2\cdot^- \rightarrow R_2CHOO:^- \quad (6)$$

$$R_2CHOO\cdot + R_2CH:^- \rightarrow R_2CHOO:^- + R_2CH\cdot \quad (7)$$

$$R_2CHOOH \xrightarrow{OH^-} R_2CO + H_2O \quad (8)$$

In addition, various other termination steps between peroxy radicals can be formulated, for example:

$$2\ R_2CHOO\cdot \rightarrow O_2 + R_2CO + R_2CHOH \quad (9)$$

$$R_2CHOO\cdot + O_2^- \rightarrow R_2CHOO:^- + O_2 \quad (10)$$

Since very nearly 1 mole of oxygen was absorbed per mole of fluorene, Reaction 2 must nearly always be followed by Reactions 6 and/or 10. The oxygen stoichiometry excludes Reactions 3 and 9 as important processes. The favored reaction sequence involves Reactions 1 and 2 followed by 5, 7, and 10 and with a kinetic chain length of about 20.

The most compelling evidence for this mechanism is the magnitude of the catalysis observed for the nitroaromatics and the correlation of this catalysis with ESR experiments performed in the absence of oxygen. Our results suggest that the detection of electron transfer (Reaction 4) actually can be achieved as readily by oxygen absorption studies as by ESR spectroscopy.

The occurrence of Reaction 11 is discounted on the basis that the

$$R_2CHOO\cdot + R_2CH_2 \rightarrow R_2CHOOH + R_2CH\cdot \quad (11$$

oxidation of an equal molar mixture of triphenylmethane and fluorene in *tert*-butyl alcohol solution containing potassium *tert*-butoxide does not give rise to oxidation of the triphenylmethane. Of course, triphenylmethane would not be ionized under the reaction conditions. However, if Reaction 11 were important in the oxidation of fluorene itself, it would be expected that considerable co-oxidation of triphenylmethane would have occurred since triphenylmethane and fluorene have similar reactivities toward peroxy radicals (*51*).

Catalysis by nitroaromatics in carbanion oxidations was originally observed by Weissberger in the oxidation of benzoin (*13, 40, 88, 89, 90, 91, 92, 93, 95*) and more recently by Bickel and Gershmann in the oxidation of hindered phenols (*33*). However, the catalyses were interpreted differently in this prior work.

Considerable contrast exists between the types of inhibitions and catalyses observed for the oxidations of nitroalkanes in aqueous solution (*61*) and those observed in the present work. The oxidations of the nitroalkanes in aqueous solution (but not necessarily in nonaqueous solution) show all the characteristics of free-radical chain processes having long kinetic chains but lacking significant spontaneous initiation. Moreover, the reactions undergo chain branching (autocatalysis) from some reaction intermediate, possibly an intermediate hydroperoxide. Under

these conditions large rate effects are readily observed if any initiation process (even an inefficient one) can be provided or if the chain-branching intermediate can be destroyed.

In the case of the oxidation of fluorene there is no evidence that long kinetic chains are involved or that there is any significant autocatalysis. Furthermore, it appears from the lack of observable inhibition periods that there is a facile spontaneous initiation process in the presence of oxygen (Reactions 2 and 3). Thus a hydroperoxide-destroying agent (such as arsenic trioxide) has a large effect on the oxidation of nitroalkanes in aqueous solution but not upon the oxidation of fluorene in alcoholic base (*76*). In the oxidation of fluorene only efficient catalysts which are not destroyed by the basic solution can significantly increase the total rate of initiation. Apparently ferric ions or manganese dioxide do not qualify as powerful catalysts in the oxidation of fluorene (*76*), and whatever additional initiation that these reagents may provide is small compared to that provided by Reactions 2 and 3. For 2-nitropropane in aqueous base Reaction 2 is essentially nonexistent at 25° C. Because of this ferric ion, manganese dioxide and numerous other substances can provide a large percentage increase in the total rate of initiation. This increase results in drastically shortening or completely removing the induction period observed in the absence of catalysis (*61*). However, even in the oxidation of the nitroalkanes, metal ions had little effect on the oxidation rates observed after the induction periods had been passed (*61*).

Even if the oxidation of fluorene in basic solution does involve chain branching from the intermediate hydroperoxide—e.g., Reaction 12, it

$$R_2CHOOH + R_2CH:^- \rightarrow R_2CHO\cdot + OH^- + R_2CH\cdot \qquad (12)$$

follows that retardation of the oxidation rate by a hydroperoxide-destroying agent such as arsenic trioxide would be expected only if massive amounts of the agent were employed. The self-initiated rate of hydroperoxide formation is sufficient that small amounts of arsenic trioxide would soon be destroyed by reacting with the hydroperoxide.

Oxidation of Other Polyarylmethanes

A few arylmethanes have been oxidized in basic solution. Diphenylmethane has been oxidized under heterogeneous conditions on the surface of alumina impregnated with sodium methoxide (*57*), but there have been few reports of autoxidation in homogeneous solution presumably because of the difficulty in ionizing the hydrocarbon. It is reported that perinaphthalene is converted by oxygen in the presence of alcoholic base to the 1-phenalenyl radical (*59*), while dithienylmethane has been converted to the ketone under similar conditions (*17*).

In ethereal solutions triphenylmethylsodium is converted by oxygen to the alcohol and a small amount of the peroxide (*6*), whereas 1,1-di-

phenylethylpotassium is reported to be converted mainly to the alcohol and a small amount of the dimer (*96*). The oxidation of diphenylmethylsodium in liquid ammonia is reported to yield tetraphenylethane, but experimental details are not available (*94*). The disodium adduct of stilbene (*71*), the dilithium adduct of tetraphenylethylene, and the dilithium adduct of anthracene are all converted to the unsaturated system by oxygen in ethereal solvents (*38*). The dilithium adduct of 9,10-dimethylanthracene reacts with oxygen in dimethoxyethane solution to yield mainly 9,10-dimethylanthracene; however, some 9-hydroperoxy-9,10-dimethylanthracene is also formed (*38*).

A number of cyclopentadiene derivatives have been oxidized in alcohol or pyridine solutions in the presence of bases. The conversion of 9-phenylfluorene to the alcohol or hydroperoxide (*76*), indenes to indenones and other products (*76*), fluoradene to 12,12′-bifluoradenyl (*54*), and 9,9′-bifluorene to $\Delta^{9,9'}$-bifluorene (*83*) have been reported. In addition, the instability of basic solutions of 1,5-*bis*-diphenylene-1,4-pentadiene toward molecular oxygen has been mentioned (*47*), while the lithium salt of tetraphenylcyclopentadiene reacts with molecular oxygen in benzene solution to give tetracyclone (*54*). The oxidation of dihydrofulvalene derivatives has been mentioned previously (*23, 54, 74*).

We have found that by using polar, aprotic solvents such as dimethylformamide, dimethyl sulfoxide, or hexamethylphosphoramide, a number of weakly acidic polyarylmethanes, such as di- and triphenylmethane, can be readily ionized and oxidized in the presence of potassium *tert*-butoxide and other bases (*65*).

In addition to di- and triphenylmethane, the oxidations of xanthene, thiaxanthene, anthrone, phenyl-4-pyridylmethane, phenyl-2-pyridylmethane, diphenyl-1-naphthylmethane, diphenylacetonitrile, diphenylacetic acid, methyl diphenylacetate, benzhydrylamine, benzhydryl chloride, benzhydryl bromide, 1,1-diphenylacetone, and 4,5-methylenephenanthrene have been observed.

Effects of Solvent and Base. The effect of solvent and the nature of the base have been investigated in the oxidation of di- and triphenylmethane. Because many of the solvents employed react with oxygen in the presence of strong bases such as potassium *tert*-butoxide, *tert*-butyl alcohol was often employed as a diluent. Solutions of DMSO and dimethylformamide (DMF) containing 20% by volume of *tert*-butyl alcohol were essentially stable (within the reaction times involved) toward oxygen in the presence of potassium *tert*-butoxide at room temperature. Hexamethylphosphoramide (HMPA)) containing potassium *tert*-butoxide absorbed oxygen slowly but at a negligible rate compared to the rate of oxidation of most substrates. Pertinent results are summarized in Tables IV and V.

Table IV. Solvent Effects in the Oxidation of Di- and Triphenylmethane at 25° C. ± 2°[a]

Solvent[b]	Initial Rates of Oxidation[c]	
	Diphenylmethane	Triphenylmethane
tert-BuOH	0	0
Py(80)–*tert*-BuOH(20)	0.02	0.02[d]
Py[e]	0.50	0.52[f]
DMF(80)–*tert*-BuOH(20)	0.05	0.08
DMSO(80)–*tert*-BuOH(20)	1.00	1.10
HMPA(80)–*tert*-BuOH(20)	0.58	0.68
HMPA	4.80	0.30

[a] 0.1*M* Arylmethane, 0.2*M* potassium *tert*-butoxide in 25 ml. of solution, vigorously agitated in a creased flask by a wrist action shaker.
[b] *tert*-BuOH = *tert*-butyl alcohol, DMF = dimethylformamide, DMSO = dimethyl sulfoxide, HMPA = hexamethylphosphoramide, Py = pyridine.
[c] Moles oxygen/mole arylmethane per min.
[d] Rate not increased by 44% nitrobenzene based on triphenylmethane.
[e] Heterogeneous.
[f] Rate not increased by 44, 97.5, 195, or 390% of nitrobenzene based on triphenylmethane.

Table V. Effect of Structure of Base in the Oxidation of Triphenylmethane in DMSO(80%)–*tert*-Butyl Alcohol (20%) at 25° C. ± 2°[a]

Base (0.1*M*)	Initial Rates (Moles oxygen/mole $(C_6H_5)_3CH$/min.)
Lithium *tert*-butoxide	0.15
Sodium *tert*-butoxide	0.32
Potassium *tert*-butoxide	0.82
Sodium methoxide	0.20
Potassium methoxide[b]	0.006
Potassium hydroxide[c]	0.067
Potassium *tert*-butoxide[d]	1.07
Tetramethylammonium *tert*-butoxide[d]	1.10

[a] 0.1*M* Triphenylmethane in 25 ml. of solution.
[b] DMSO (80%)–methanol (20%); oxidation rate recorded after 70 min. induction period.
[c] Saturated solution.
[d] 0.2*M*.

Dimethyl sulfoxide and HMPA were superior solvents, while tetramethylammonium and potassium *tert*-butoxide were the most efficient bases investigated in DMSO solution. The potency of a base-solvent system is presumably determined by the ionization rate of the hydrocarbon to the carbanion and is connected with the dielectric constant of the system, the solvation of the cation, and hydrogen bonding that can reduce the activity of the alkoxide anion. The solvent and bases studied were ineffective at room temperature in the ionization and oxidation of simple alkylbenzenes or olefins, such as toluene, ethylbenzene, cumene, or cyclohexene. However, the simple alkylnaphthalenes and a variety of alkyl-substituted heteroaromatics are readily oxidized.

The product of the oxidation of triphenylmethane was the carbinol. A 95–97% yield was isolated from the oxidation in DMSO(80%)–*tert*-butyl alcohol(20%), while a quantitative amount of diphenyl-1-naphthylcarbinol was obtained from the oxidation of diphenyl-1-naphthylmethane under the same conditions. Approximately 1 mole of oxygen

per mole triphenylmethane was absorbed at complete reactions in all oxidations in DMSO(80%)–*tert*-butyl alcohol(20%) and HMPA(80%)–*tert*-butyl alcohol(20%) solutions.

Benzhydrol was the initial product isolated from the oxidation of diphenylmethane in DMSO(80%)–*tert*-butyl alcohol (20%) in 60–75% yield. Prolonged oxidation, particularly in the presence of large amounts of base, led to the DMSO addition product of benzophenone (*65*), ($(C_6H_5)_2C(OH)CH_2SOCH_3$) isolated in 63% yield. The oxygen stoichiometry varied from 1 to 3 moles of oxygen per mole diphenylmethane depending on the solvent used. A significant decrease in the oxidation rate occurred when approximately 1.0–1.2 moles of oxygen per mole of diphenylmethane had been absorbed in DMSO(80%)–*tert*-butyl alcohol(20%) solutions; the maximum yields of benzhydrol could be isolated if the oxidations were interrupted at this time. In this solvent approximately 3 moles of oxygen were absorbed per mole of diphenylmethane at complete reaction. Since the oxidation of benzhydrol to benzophenone requires approximately 2 moles of oxygen per mole of benzhydrol in this solvent, the conversion of diphenylmethane to benzhydrol involves the absorption of about 1 mole of oxygen per mole of diphenylmethane.

Electron transfer from the di- or triphenylmethide anion to nitrobenzene to produce nitrobenzene radical-anions, can be readily detected by ESR in DMSO(80%)–*tert*-butyl alcohol(20%) solutions (*62, 63*), while in the reaction of fluorenes with traces of oxygen in the presence of strong bases the corresponding ketyl radical-anions were detected. Attempts to detect radical intermediates from the initial reaction of di- and triphenylmethane with traces of oxygen in DMSO(80%)–*tert*-butyl alcohol(20%) or in pure DMSO solutions containing potassium *tert*-butoxide have been unsuccessful. This is presumably caused by the reactivity of the di- and triphenylmethyl radicals and the low concentration of benzhydrol in the oxidation reaction of diphenylmethane at the time of the ESR experiment. Benzhydrol in pure DMSO in the presence of excess potassium *tert*-butoxide does produce significant amounts of benzophenone ketyl when treated with deficient quantities of oxygen; the exposure of tris(*p*-nitrophenyl)methane to molecular oxygen in basic solution produces considerable amounts of the tris(*p*-nitrophenyl)methyl radical.

The oxidations of di- and triphenylmethane show surprisingly small rate differences in the various solvent systems employed, although the acidities of the two hydrocarbons supposedly differ by about two pK_a units (*52, 77, 79*). Electron transfer from diphenylmethane in basic solution to nitrobenzene or azobenzene is actually faster than the electron transfer from triphenylmethane (*64*). This process reflects the ease of ionizing the hydrocarbons as well as the ease of losing one electron from the resulting carbanion.

The rate of deuterium-hydrogen exchange of α-deuteriotriphenylmethane in DMSO(80%)–*tert*-butyl alcohol(20%) containing excess potassium *tert*-butoxide occurs at about the same rate as the oxidation under similar conditions (*65*). It thus appears that the slow step in the oxidation sequence is ionization of the arylmethane. The absence of catalysis in pyridine solution by electron transfer agents, such as nitrobenzene (Table IV) and the changes in rate connected with the nature of the base and structure of the solvent (Tables IV and V) are all in accord with this conclusion. Table VI demonstrates that at low concentrations

Table VI. Oxidation of Triphenylmethane in Dimethyl Sulfoxide(80%)–*tert*-Butyl Alcohol(20%) Solutions at 26° C.

Triphenylmethane[a]	*KOCMe₃*[a]	O_2 *Pressure*	k_1[b]	$k_i = k_1/[B^-]$
0.025	0.05	749	0.0070	0.140
0.025	0.10	749	0.0103	0.103
0.025	0.20	749	0.0340	0.169
0.049	0.135	749	0.0213	0.158
0.049	0.0905	749	0.0116	0.128
0.050	0.20	749	0.0296	0.148
0.100	0.20	749	0.0341	0.171
0.025	0.05	609	0.00725	0.145
0.025	0.05	402	0.0082	0.164
0.025	0.05	760	0.0075	0.151[d]
0.100	0.20	749	0.0257	0.128[e]

[a] Moles/liter.
[b] Sec.$^{-1}$
[c] Liter/mole-sec.
[d] In presence of 0.098*M* nitrobenzene.
[e] In presence of 0.39*M* nitrobenzene.

of base and hydrocarbon, the oxidation rate of triphenylmethane is independent of oxygen pressure (above 400 mm.) or presence of nitrobenzene. It thus appears that under the conditions of Table VI, we have the limiting situation wherein every triphenylmethide ion formed is immediately consumed by reaction with molecular oxygen or some other reaction intermediate. Thus, the rate of oxygen absorption measures the rate of ionization.

$$(C_6H_5)_3CH + RO^- \xrightarrow{\text{slow},\ k_i} (C_6H_5)_3C{:}^- + ROH$$

$$(C_6H_5)_3C{:}^- + O_2 \xrightarrow{\text{fast}} (C_6H_5)_3CO^-\ (RO^-)$$

Figure 7 gives a typical pseudo first-order plot for the oxidation of triphenylmethane at constant concentration of base ($[RH]_t = [RH]_o - O_2$ absorbed). Values of the pseudo first-order rate constants (k_1) observed at various reactant concentrations are summarized in Table VI. Some typical ionization rates measured in this manner are summarized in Table VII.

A free-radical oxidation mechanism is preferred for the oxidation of the polyarylcarbanions particularly in view of the evidence presented for

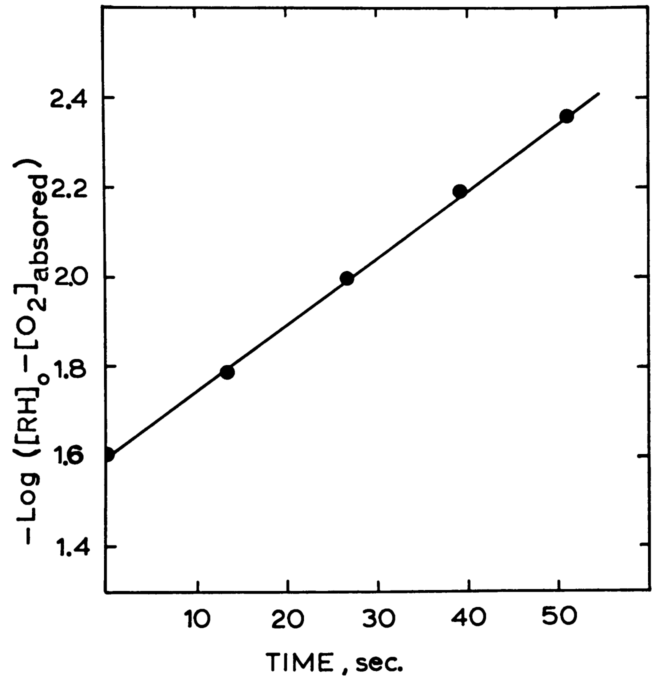


Figure 7. Pseudo first-order kinetic relationship observed in the autoxidation of triphenylmethane (initial concentration 0.025M) at 24.5°C. in a solution initially 0.20M potassium tert-*butoxide in DMSO(80%)*—tert-*butyl alcohol-(20%)*

such a mechanism in the oxidation of fluorene in basic solution. However, because of the differences in the acidities of the parent hydrocarbons (fluorene, $pK_a = 25$; triphenylmethane, $pK_a = 33$; diphenylmethane, $pK_a = 35$) (52) and differences in reactivity between the fluorenide anion and the di- or triphenylmethide anions toward molecular oxygen, the catalysis of the oxidation of the polyarylmethide anions observed for fluorene is more difficult to observe for di- and triphenylmethane. The fast oxidation reactions are imagined to be those below.

$$R:^- \xrightarrow{O_2} R\cdot + O_2\cdot^-$$

$$R:^- \xrightarrow{ROO\cdot} ROO^- + R\cdot$$

$$R\cdot + O_2 \rightarrow ROO\cdot$$

$$ROO^- + DMSO \rightarrow RO^- + DMSO_2$$

Among the possible termination steps are:

$$ROO\cdot + O_2\cdot^- \rightarrow ROO:^- + O_2$$

$$ROO\cdot + R\cdot \rightarrow ROOR$$

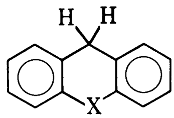
In the oxidation of triphenylmethane a termination reaction involving the triphenylmethyl radical is possible even in solutions saturated with oxygen at 1 atmosphere (*36*).

Table VII. Rates of Ionization of Carbon Acids by *tert*-Butoxide Ion at 24.5° C.

Hydrocarbon	*Solvent*	k_i (*Liters/ Mole-Sec.*)
Triphenylmethane	DMSO(80)-*tert*-BuOH(20)	0.134 ± 0.003
Triphenylmethane	DMSO(70)-*tert*-BuOH(30)	0.038 ± 0.003
Triphenylmethane	DMSO(60)-*tert*-BuOH(40)	0.012 ± 0.001
Triphenylmethane-α-*d*	DMSO(80)-*tert*-BuOH(20)	0.018 ± 0.001
Diphenyl-α-naphthylmethane	DMSO(80)-*tert*-BuOH(20)	0.163 ± 0.018
Diphenylmethane	DMSO(80)-*tert*-BuOH(20)	0.085 ± 0.015[a]

[a] k_i calculated from initial rate of oxidation.

Effects of Structure of Arylmethanes on Rate and Stoichiometry of Oxidation. The initial rates of oxidation, oxygen stoichiometry, and oxidation products of a series of cyclic derivatives of diphenylmethane,



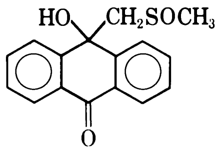
where X = O, S, and CO, were measured in DMSO(80%)–*tert*-butyl alcohol(20%) in the presence of potassium *tert*-butoxide. Pertinent data are summarized in Table VIII. The oxidation rate of all the diphenylmethane derivatives, except for anthrone, were significantly faster than for diphenylmethane itself probably because of the increased acidity of the methylene protons (e.g., xanthene $pK_a = 29$) (52). Ionization of anthrone yields a phenoxide ion that is relatively stable to oxygen. 9-Nitroanthrone was completely stable to oxygen under the reaction conditions.

Anthrone oxidized in basic solution to anthraquinone (which reacts further with the solvent) with an oxygen stoichiometry of 1 mole per mole anthrone. Thus, the intermediate hydroperoxides formed from fluorene and anthrone are decomposed by base to give the ketones (*22, 46*), whereas the intermediate hydroperoxides derived from diphenylmethane.

$$R_2CHOOH + B^- \rightarrow R_2CO + BH + OH^-$$

and to a lesser extent xanthene and thiaxanthene, are converted to the alcohols, whose ultimate oxidation to the ketone results in an overall oxygen stoichiometry considerably greater than 1 mole per mole of active methylene compound. The base-catalyzed decomposition of the hydroperoxides derived from fluorene and anthrone, but not from diphenylmethane, is undoubtedly connected with the greater acidity of the α-hydrogen atoms in the fluorene and anthrone hydroperoxides.

In DMSO(80%)–*tert*-butyl alcohol(20%) containing potassium *tert*-butoxide, anthraquinone is converted to mono-adduct of DMSO at room temperature.



This product was obtained in 68% yield in the oxidation of anthrone and in 88% yield from anthraquinone in similar solutions in the absence of oxygen.

Adducts of xanthenone and thiaxanthenone were not isolated from DMSO under similar conditions. The oxygen stoichiometry for xanthene and thiaxanthene suggest mechanisms involving intermediate hydroperoxides that are in part converted directly to the ketones and in part converted to alcohols that are further oxidized to the ketones. The intermediate alcohols could not be isolated because they oxidize easily. However, considerable amounts of the ketyl radical-anions could be detected in oxidations with deficient quantities of the oxygen.

Oxidation of Nitroalkanes

The autoxidation of 2-nitropropane has been studied previously in aqueous basic solutions and less thoroughly in the presence of alcoholic base (*61*). The prior work demonstrated a free-radical chain mechanism formulated as follows;

$$(CH_3)_2C = NO_2^- + ROO\cdot \rightarrow ROO{:}^- + (CH_3)_2\dot{C}NO_2\ (R\cdot) \qquad (13)$$

$$R\cdot + O_2 \rightarrow ROO\cdot \qquad (14)$$

$$R{:}^- + ROOH \rightarrow RO{:}^- + ROH \qquad (15)$$

$$RO{:}^- \rightarrow CH_3COCH_3 + NO_2^- \qquad (16)$$

$$\overline{(CH_3)_2C = NO_2^- + {}^1/_2\,O_2 \rightarrow CH_3COCH_3 + NO_2^-}$$

In aqueous basic solution the reaction has a significant induction period followed by a sharply autocatalytic oxidation. The inhibition period can be removed by certain metal ions, whereas the inhibition period can be prolonged for extremely long periods of time by the presence of the hydroperoxide-destroying agent, arsenic trioxide. These results lead to the following conclusions:

(a) The 2-nitro-2-propyl anion does not undergo a direct reaction with molecular oxygen in aqueous basic solution;

(b) The chain-branching agent responsible for the autocatalytic oxidation involves an intermediate hydroperoxide, presumably 2-nitro-2-propyl hydroperoxide;

Table VIII. Oxidation of Cyclic Diphenylmethanes at 25° C. ± 2°[a]

	Initial Rate[b]	*Oxygen Absorbed*[c]	*Products (Yield)*
Fluorene	4.4	1.0	fluorenone-DMSO adduct (75%)
Anthrone	0.8	1.02	anthraquinone (13%), anthraquinone-DMSO adduct (68%)
Xanthene	4.5	1.68	xanthone (92%)
Thiaxanthene	3.0	1.21	thioxathone (51%)
Diphenylmethane	1.0	1.27 (5.6 min.)	benzhydrol (75%)
Diphenylmethane	1.0	3.00 (30 min.)	benzophenone-DMSO adduct (63%)
Phenyl-4-pyridylmethane	4.1	1.46	
Phenyl-2-pyridylmethane	2.6	1.26	
4,5-Methylenephenanthrene	3.7	1.32	4-phenanthroic acid (low)

[a] 0.1*M* Diphenylmethane derivative, 0.22*M* potassium *tert*-butoxide in 25 ml. DMSO(80%)–*tert*-butyl alcohol (20%).
[b] Moles oxygen/mole substrate per min.
[c] Moles oxygen/mole substrate at complete oxidation.

(c) Long kinetic chains are involved.

It also was found that in the presence of large excesses of hydroxide ion in aqueous solution or an equivalent or greater amount of ethoxide ion in ethanol, the maximum rate of oxidation was diminished considerably. In the case of ethanol the rapid oxidation observed in the presence of a slight deficiency of base essentially stopped completely in the presence of a slight excess of ethoxide ion. We now prefer to interpret these results as indicating an initiation reaction by electron transfer between the 2-nitropropane anion and unionized 2-nitropropane. The initiation reactions and chain-branching reactions in the oxidation are formulated below.

$$R:^- + (CH_3)_2CHNO_2 \rightarrow R\cdot + (CH_3)_2CHNO_2\cdot^- \xrightarrow{O_2} (CH_3)_2CHNO_2 + O_2\cdot^- \quad (17)$$

$$R:^- + ROOH \rightarrow R\cdot + RO\cdot + OH^- \quad (18)$$

We now have extended the investigation to other solvent systems and have investigated the role of catalysis by electron transfer more thoroughly in the oxidation of 2-nitropropane as well as *p*-nitrotoluene, and tris(*p*-nitrophenyl)methane.

Effect of Concentration of Base on Oxidation of 2-Nitropropane. The effect of the ratio of base to 2-nitropropane has been investigated in *tert*-butyl alcohol, pyridine, DMSO(80%)–*tert*-butyl alcohol(20%) solvents (Figure 8), and in ethanol (Figure 9). In all cases a maximum in the oxidation rate is observed at ratios of base to 2-nitropropane between 0.5 (ethanol) and about 2 (*tert*-butyl alcohol).

In nonaqueous solvents the reaction appears to follow the same course as in aqueous solution except that in some of the solvents the initially formed acetone is converted to carboxylic acids. Some typical results are shown in Table IX.

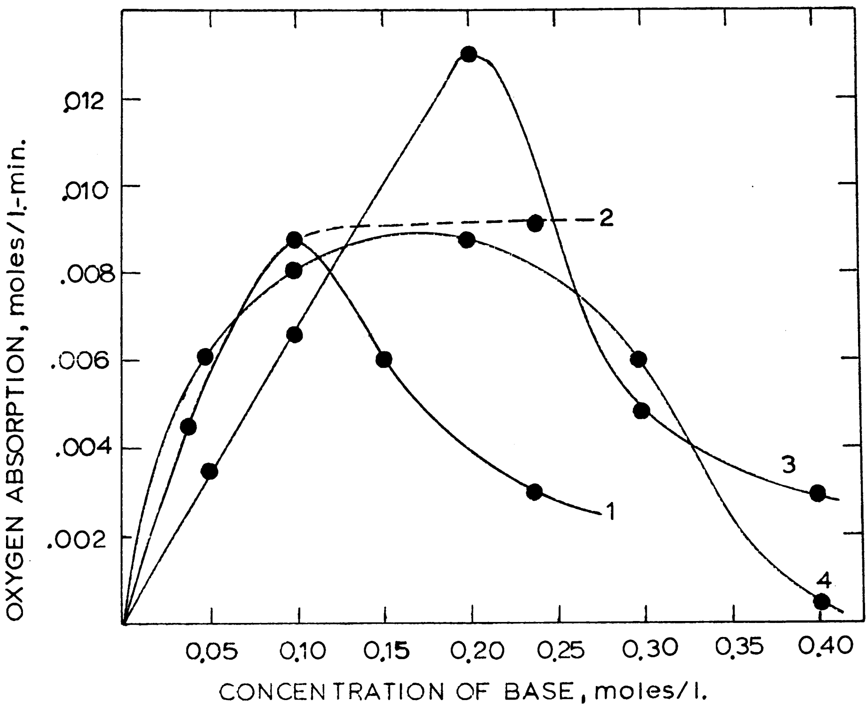


*Figure 8. Initial (maximum) rates of oxidation of 0.1*M *2-nitropropane; (1) potassium* tert-*butoxide in dimethyl sulfoxide (80%)–*tert-*butyl alcohol (20%); (2) conditions 1 plus 0.12*M *nitrobenzene; (3) lithium* tert-*butoxide in pyridine; (4) lithium* tert-*butoxide in* tert-*butyl alcohol*

In ethanol containing lithium ethoxide about one-half mole of oxygen is absorbed per mole of base in the presence of excess 2-nitropropane. In the presence of excess lithium ethoxide no reaction occurs except when catalyzed by *m*-dinitrobenzene whence the initially formed acetone is extensively oxidized. In *tert*-butyl alcohol containing lithium *tert*-butoxide one-half mole of oxygen is absorbed per mole of 2-nitropropane oxidized with an essentially quantitative yield of acetone. In this system acetone is not appreciably oxidized in the presence of excess base. In *tert*-butyl alcohol containing potassium *tert*-butoxide about one-half mole of oxygen is absorbed per mole of base in the presence of excess 2-nitropropane, while in the presence of excess base the acetone is extensively oxidized to carboxylic acids. The same stoichiometry is observed whether or not nitrobenzene is added as a catalyst. In pyridine solutions containing lithium *tert*-butoxide or Triton B (benzyltrimethylammonium methoxide), or DMSO(80%)–*tert*-butyl alcohol(20%) containing potassium *tert*-butoxide, the initially formed acetone is extensively oxidized. In these solvent systems a high oxygen stoichiometry is observed even in the

presence of deficient base. Possibly the intermediate peroxy radical or anion reacts with the solvent, or acetone is oxidized more readily than

$$\text{ROO}\cdot\ (\text{or ROO:}^-) + \text{S} \rightarrow \text{RO}\cdot\ (\text{or RO}^-) + \text{SO} \quad (19)$$

2-nitropropane. In these solvents about a mole of oxygen is required to neutralize a mole of the starting base. (In DMSO(80)-*tert*-BuOH(20) this result is analogous to the observation that triphenylmethane is converted quantitatively to triphenylcarbinol with the absorption of one mole of oxygen.)

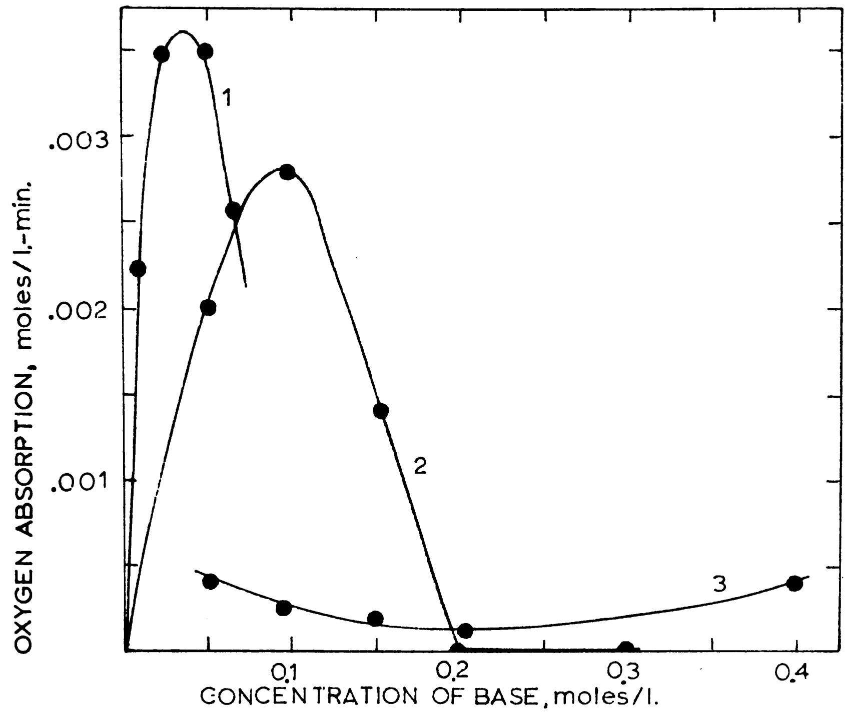


*Figure 9. Oxidation of 2-nitropropane; (1) 0.05*M *2-nitropropane, benzyltrimethylammonium methoxide in pyridine; (2) 0.2*M *2-nitropropane, lithium ethoxide in ethanol; (3) in presence of 0.12*M m*-dinitrobenzene*

Inhibition and Catalysis of the Oxidation of 2-Nitropropane. Arsenic trioxide inhibits the oxidation of 2-nitropropane in the presence of alcoholic base as well as in aqueous solution (*61*). Some typical results are shown in Figure 10. However, the efficiency of arsenic trioxide is greatly reduced in alcoholic solution suggesting a more facile spontaneous initiation reaction than in aqueous solutions. The results are consistent with Reaction 17's being slow in aqueous solution but quite rapid in alcoholic solution. In the presence of excess base arsenic trioxide is a more efficient inhibitor in accord with the assumption that spontaneous initia-

Table IX. Products and Stoichiometry

Solvent	Base (Moles/Liter)	2-Nitropropane (Moles/Liter)	Oxygen Moles/Moles 2-Nitropropane
EtOH	LiOEt (0.096)	0.20	
EtOH + 0.12*M* *m*-dinitrobenzene	LiOEt (0.40)	0.20	0.44 (361 min.)[b] 1.14 (60 hrs.)
tert-BuOH	$LiOCMe_3$ (0.10)	0.10	0.45
tert-BuOH	$LiOCMe_3$ (0.20)	0.10	0.60
tert-BuOH	$LiOCMe_3$ (0.33)	0.16	0.54
tert-BuOH	$LiOCMe_3$ (0.16)	0.44	
tert-BuOH	$KOCMe_3$ (0.08)	0.20	
tert-BuOH	$KOCMe_3$ (0.35)	0.44	
tert-BuOH	$KOCMe_3$ (0.20)	0.20	0.36
tert-BuOH	$KOCMe_3$ (0.50)	0.20	1.01
tert-BuOH	$KOCMe_3$ (1.0)	0.20	1.5 (55 min.)
tert-BuOH + 0.12*M* nitrobenzene	$KOCMe_3$ (1.0)	0.20	1.64 (36 min.)
tert-BuOH	$KOCMe_3$ (0.50)	0.20	1.0[b] 1.66
tert-BuOH + 0.12*M* nitrobenzene	$KOCMe_3$ (0.50)	0.20	1.0[b] 1.9
Pyridine	$LiOCMe_3$ (0.29)	0.48	
Pyridine	$LiOCMe_3$ (0.29)	0.30	1.4
Pyridine	$LiOCMe_3$ (0.40)	0.10	1.2
Pyridine	Triton B (0.10)	0.03	1.4
Pyridine	Triton B (0.048)	0.056	1.1
Pyridine	Triton B (0.026)	0.078	
DMSO(80)-*tert*-BuOH(20)	$KOCMe_3$ (0.04)	0.10	
DMSO(80)-*tert*-BuOH(20)	$KOCMe_3$ (0.15)	0.10	1.40
DMSO(80)-*tert*-BuOH(20) + 0.12 *M* nitrobenzene	$KOCMe_3$ (0.15) $KOCMe_3$ (0.24)	0.10 0.10	1.40 2.00

[a] All experiments involved 25 ml. of solution at room temperature ~25°C.
[b] Incomplete oxidation.
[c] Moles/mole base.

tion involves Reaction 17 and that this process is retarded at high concentrations of base wherein the concentration of unionized 2-nitropropane is quite low.

Further evidence in favor of a radical-chain oxidation of 2-nitropropane is provided by the effect of various nitroaromatics on the reaction rate. Figures 8 and 9 demonstrate catalytic effects of nitrobenzene and *m*-dinitrobenzene in DMSO(80%)-*tert*-butyl alcohol(20%) and ethanol solutions, respectively. These results are consistent with an initiation reaction by the catalyst of the type:

$$R:^- + ArNO_2 \rightarrow R\cdot + ArNO_2\cdot^- \qquad (20)$$

This electron transfer reaction has been observed in the absence of oxygen by ESR spectroscopy between the 2-nitro-2-propyl anion and nitrobenzene or *m*-dinitrobenzene (*63*). In the case of *m*-dinitrobenzene, catalysis is observed in ethanol solution at high base concentration where the spontaneous initiation reaction—Reaction 17—apparently does not occur. However, at lower base concentrations where the spontaneous initiation reac-

of Oxidation of 2-Nitropropane[a]

Absorbed	Products (Moles/Mole 2-Nitropropane			
Moles/Mole Base	Acetone	Carboxylic Acids	Nitrite Ion	Nitrate Ion
0.58				
	0.20	0.71	0.94	0.01
0.45				
0.44	1.0[c]			
0.52				
0.50				
0.36				
0.40				
0.19	0.80	0.96	<0.01	
0.14				
0.24	0.91	0.90	<0.02	
0.20				
1.4				
1.4				
2.2				
0.8				
0.93				
0.93				
0.83				

tion does occur, *m*-dinitrobenzene has the overall effect of inhibiting the oxidation reaction (Figure 9). Table X summarizes other initiation and retardation effects observed in the oxidation of 2-nitropropane.

The ability of the unsaturated electron transfer agents to catalyze the reaction (e.g., nitrobenzene, azobenzene) parallels their ability to undergo one-electron transfer with a wide variety of carbanions (*63*). All of the catalysts reported in Table IX and Figures 8 and 9 were either stable to oxygen in the basic solvent systems employed or gave negligible blanks.

Catalysis of the Oxidation of *p*-Nitrotoluene and Derivatives. Since Reaction 17, or a similar process, is involved in the oxidation of *p*-nitrotoluene and derivatives in basic solution (*62*), it should be possible to provide additional catalysis for these oxidations via Reaction 20. Figure 11 shows that *m*-dinitrobenzene will catalyze the slow oxidation of *p*-nitrotoluene observed in *tert*-butyl alcohol-methanol mixtures containing potassium alkoxide as the base. Here there is only a small degree of ionization of the *p*-nitrotoluene, and the oxidation is catalyzed by the presence

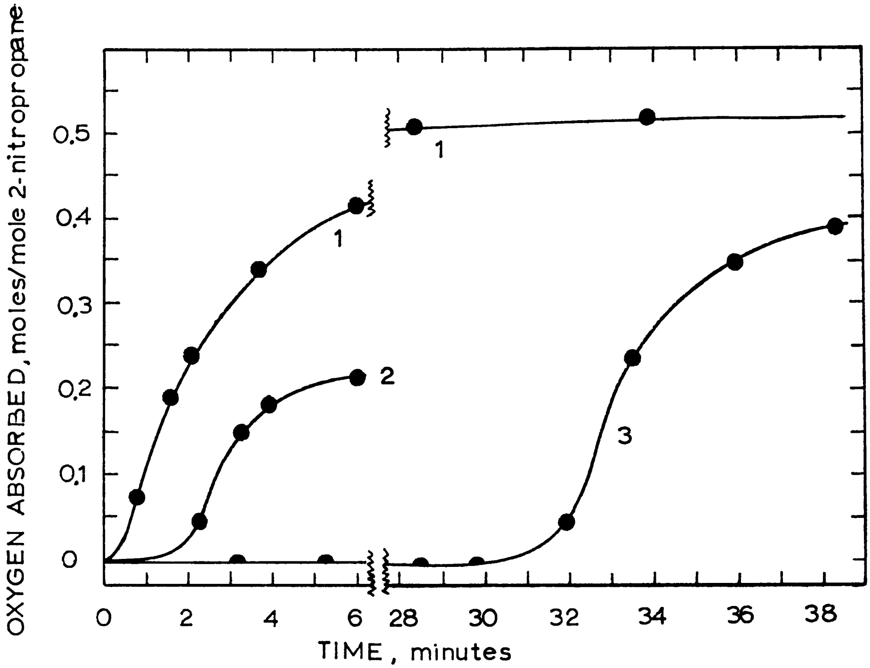


*Figure 10. Autoxidation of 0.16*M *2-nitropropane in* tert-*butyl alcohol containing 0.33*M *lithium* tert-*butoxide; (1) no additive; (2) 0.01*M *As_2O_3; (3) 0.07*M *As_2O_3*

Table X. Rates of Catalyzed and Inhibited Oxidations of 2-Nitropropane in Basic Solution[a]

Catalyst or Inhibitor (Moles/Liter)	*Base (Moles/Liter)*	*Inhibition Period (Min.)*	*Maximum Oxidation Rate*[b]
None	$KOCMe_3$ (0.2)	...	0.020
p-$NCC_6H_4NO_2$ (0.01)	$KOCMe_3$ (0.2)	...	0.067
$C_6H_5NO_2$ (0.12)	$KOCMe_3$ (0.2)	...	0.057
Anthraquinone (0.12)	$KOCMe_3$ (0.2)	...	0.053
Azoxybenzene (0.12)	$KOCMe_3$ (0.2)	...	0.027
Azobenzene (0.12)	$KOCMe_3$ (0.2)	...	0.024
None[c]	$LiOCMe_3$ (0.13)	...	0.10
As_2O_3 (0.009)[c]	$LiOCMe_3$ (0.13)	1.5	0.12
As_2O_3 (0.011)[c]	$LiOCMe_3$ (0.13)	2.5	0.10
As_2O_3 (0.013)[c]	$LiOCMe_3$ (0.33)	30.0	0.08
As_2O_3 (0.08)[c]	$LiOCMe_3$ (0.13)	3900.0	[d]

[a] 0.20*M* 2-Nitropropane in *tert*-butyl alcohol.
[b] Moles oxygen absorbed/mole 2-nitropropane per minute.
[c] 2-Nitropropane = 0.16*M*.
[d] Experiment discontinued.

of a better electron acceptor than *p*-nitrotoluene itself. The products of the reaction are a mixture of *p*-nitrobenzoic acid and *p,p'*-dinitrobibenzyl, the same products observed in the rapid uncatalyzed reaction occurring in potassium *tert*-butoxide in *tert*-butyl alcohol solutions (*62*). A some-

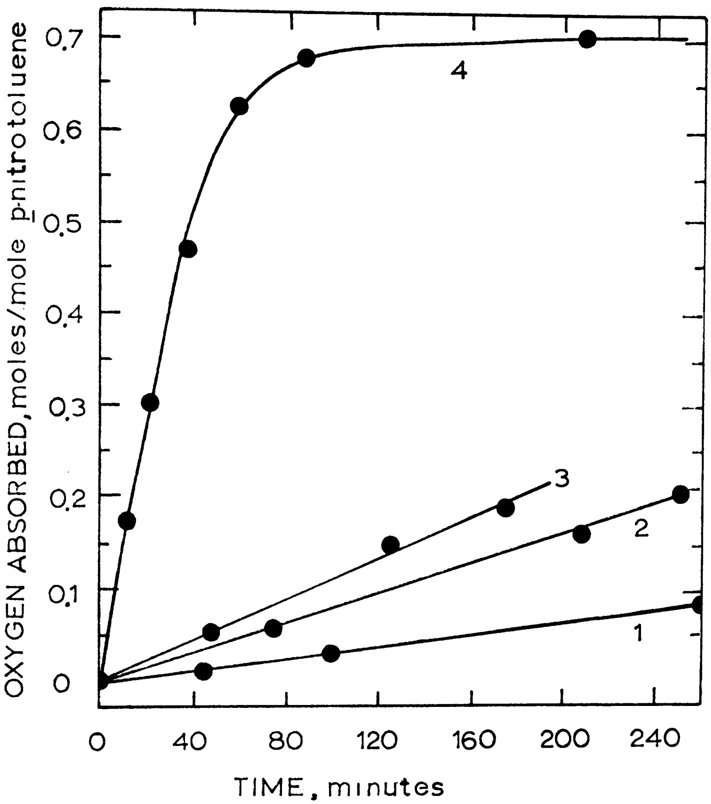


Figure 11. Oxidation of p-*nitrotoluene in* tert-*butyl alcohol (80%)–methanol (20%), 0.45*M *potassium alkoxide, 0.145*M p-*nitrotoluene; (1) no additive; (2) 0.12*M *azobenzene; (3) 0.12*M *anthraquinone; (4) 0.12*M m-*dinitrobenzene*

what similar situation exists in the oxidation of tris(*p*-nitrophenyl)-methane. This oxidation has previously been examined and found to yield mainly the carbinol (*35*). Figure 12 shows that in ethanol containing potassium hydroxide, oxidation is faster at lower ratios of base to tris(*p*-nitrophenyl)methane (compare curves 1 and 2). Moreover, the presence of an excess of a more powerful base (potassium *tert*-butoxide in *tert*-butyl alcohol) causes the rate to decrease severely (compare curves 2 and 4). Here catalysis involves the presence of unionized tris(*p*-nitrophenyl)methane, and increasing the concentration or basicity of the base employed can retard the oxidation rate by reducing the amount of unionized tris(*p*-nitrophenyl)methane present at equilibrium. (Figure 11 also illustrates catalysis by ferric salts. Ferric salts apepar to catalyze carbanion oxidations when there is not some other rapid initiation reaction, e.g., 2-nitropropane in aqueous base, or tris(*p*-nitrophenyl)methane in the

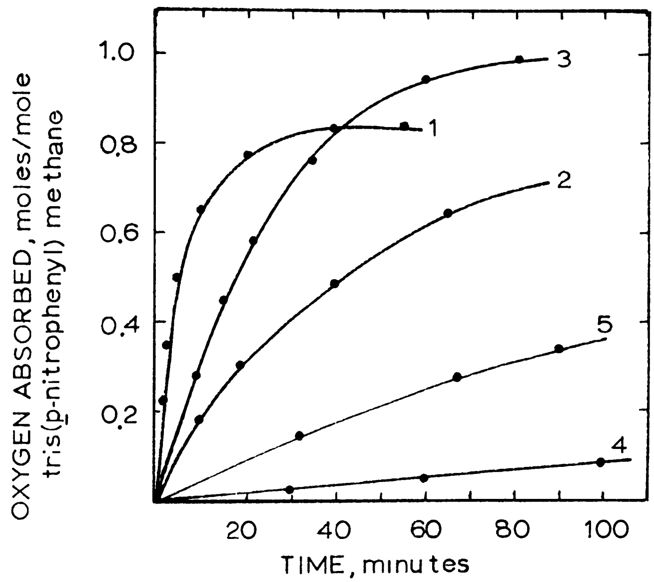


*Figure 12. Oxidation of tris(*p*-nitrophenyl)methane at 26°C.; (1) 0.02*M *tris(*p*-nitrophenyl)methane, 0.35*M *potassium hydroxide in ethanol; (2) 0.08*M *tris(*p*-nitrophenyl)-methane, 0.70*M *potassium hydroxide in ethanol; (3) condition 2 plus 0.001*M *ferric chloride; (4) 0.12*M *tris(*p*-nitrophenyl)methane, 0.35*M *potassium* tert-*butoxide in* tert-*butyl alcohol; (5) condition 4 plus 0.001*M *ferric chloride*

Table XI. Initial Rates of Oxidation of tris(*p*-Nitrophenyl)Methane

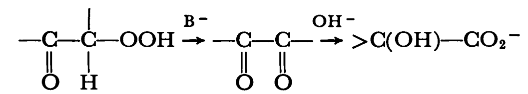
Solvent	*Concn. of Tris-(p-Nitrophenyl)-Methane, Moles/Liter*	*Concn. of Potassium tert-Butoxide, Moles/Liter*	*Initial Rate of Oxidation, Moles/Liter-Min.*
tert-BuOH	0.033	0.033	0.00023
tert-BuOH	0.033	0.100	0.00005
tert-BuOH + 0.33*M* nitrobenzene	0.033	0.100	0.00041
DMSO(80)-*tert*-BuOH(20)	0.100	0.050	0.10
DMSO(80)-*tert*-BuOH(20)	0.100	0.195	0.03

presence of excess base. On the other hand if a rapid initiation reaction is available ferric chloride has little effect. In *tert*-butyl alcohol containing potassium *tert*-butoxide the rate of oxidation of 9-fluorenol is slightly retarded (deficient potassium *tert*-butoxide). No effect is observed on the rate of oxidation of phenylacetonitrile and diphenylacetonitrile while the oxidation of benzyl alcohol and benzhydrol under conditions not involving carbanions, are drastically retarded.) Similar effects of the concentration and strength of the base employed have been observed in the electronic disporportionation of substituted *p*-nitrotoluenes in basic solutions

in the absence of oxygen (*62*). Table XI presents some additional evidence of the effect of base concentration on the oxidation rate of tris(*p*-nitrophenyl)methane as well as an additional example of catalysis by nitrobenzene.

Oxidation of Ketones

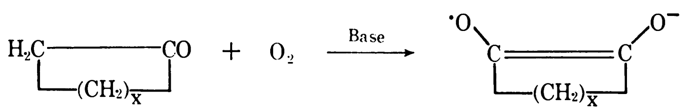
The oxidation in basic solution of saturated ketones produces α-hydroperoxy ketones (*8, 9*), α-diketones (or their enolic analogues), products of their benzylic acid rearrangement (*3, 12, 18, 19, 34*), or various products in which a carbon—carbon bond has been broken (*4, 10, 24, 25, 45*).



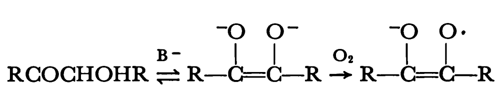
$$RCOCHROOH \xrightarrow{B^-} RCO_2H + RCHO$$

The oxidation of phenones gives good yields of benzoic acid (*10, 24*), with no evidence of an initiation reaction similar to Reactions 17 and/or 18 since inhibition periods or autocatalysis are not observed. However, this work presents strong evidence in favor of a carbanion-radical chain process with a facile initiation process involving molecular oxygen (Reactions 2 and 3).

Detection of Paramagnetic Products in the Oxidation of Phenones. A number of alicyclic and aliphatic ketones give rise to radical-anions of 1,2-diketones when exposed to traces of oxygen in basic solution (*66, 67*).



The formation of aliphatic semiquinones of this type is particularly easy for a number of phenones of the type $C_6H_5COCH_2R$. Although acetophenone, *p*-hydroxyacetophenone, or *p*-aminoacetophenone do not produce an intermediate or by-product readily detectable by ESR spectroscopy under various conditions, the semiquinone anions are readily detected by reaction of traces of oxygen with desoxybenzoin, propiophenone (Figure 13), *p*-chloropropiophenone, *p*-methoxypropiophenone, *n*-butyrophenone (Figure 14), *p*-chlorobutyrophenone, 1-(2-thienyl)-1-propanone, and 1-(2-thienyl)-1-butanone in DMSO(80%)–*tert*-butyl alcohol(20%) containing an excess of potassium *tert*-butoxide. The semiquinones can also be prepared by oxidizing the corresponding α-hydroxyketones (*66, 67*).



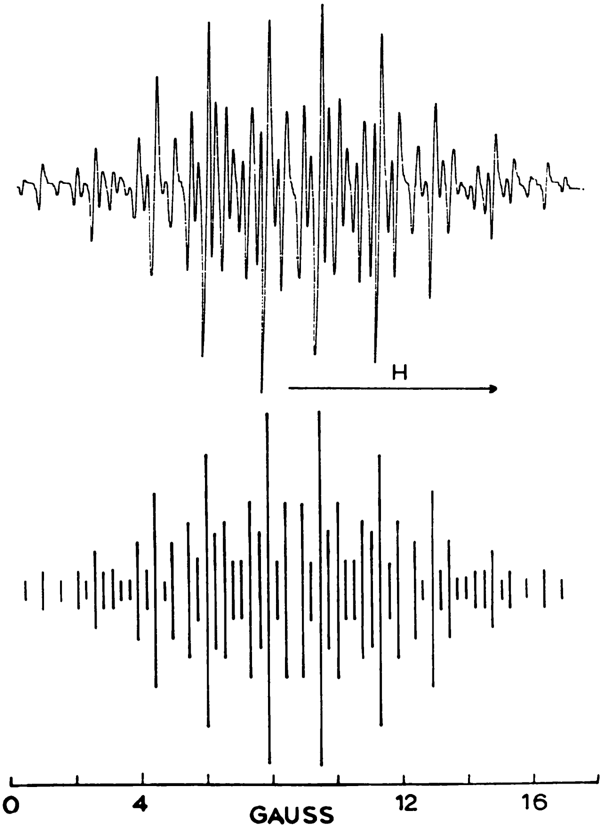


*Figure 13. ESR first derivative spectrum (~9,500 Mc./sec.) of the radical-anion of 1-phenyl-1,2-propanedione in DMSO (80%)-*tert*-butyl alcohol (20%) containing excess potassium* tert*-butoxide prepared by (a) the oxidation of propiophenone, (b) the oxidation of α-hydroxypropiophenone, or (c) spontaneously from 1-phenyl-1,2-propanedione*

The semiquinones are also formed by the disproportionation of α-hydroxyketones and 1,2-diketones in basic solution,

$$\mathrm{RCOCH(OH)R + RCOCOR \overset{B^-}{\rightleftharpoons} 2\,RC(O^-){=}C(O\cdot)R}$$

as well as from the reduction of 1,2-diketones by various methods (*62, 63*). 1,2-Diketones containing an α-hydrogen atom are a special case since in basic solution the resulting carbanion can reduce the starting diketone.

$$\text{—COCOCH<} \xrightarrow{B^-} [\text{—COCOC<}]^-$$

$$[\text{—COCOC<}]^- + \text{—COCOCH<} \rightarrow \text{—COCO}\dot{\text{C}}\text{<} + \text{—}\underset{\cdot\text{O}}{\overset{|}{\text{C}}}\text{=}\underset{\text{O}^-}{\overset{|}{\text{C}}}\text{—CH<}$$

This type of behavior is now recognized to occur for numerous *o*- and *p*-nitrotoluene derivatives (*62*), methylanthraquinone, and 1,4-dimethyltetrazine (*80*), as well as for 1-phenyl-1,2-propanedione.

Because of the multiple pathways by which an aliphatic semiquinone can be formed in the oxidation of a ketone in basic solution, it is im-

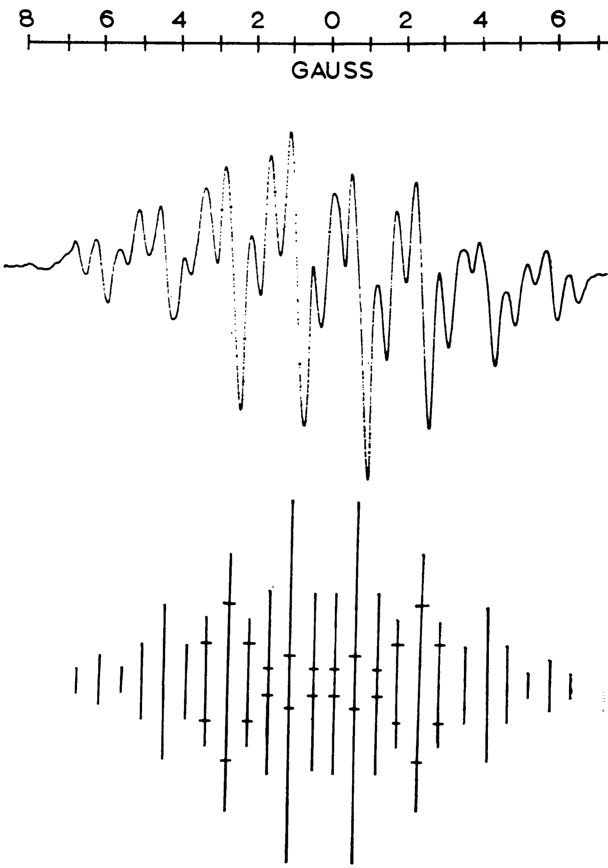
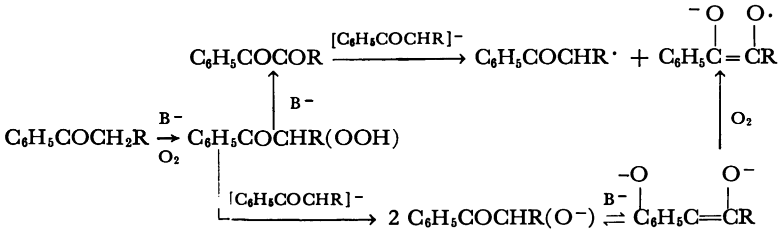


*Figure 14. ESR first derivative spectrum (~9,500 Mc./sec.) of the radical-anion of 1-phenyl-1,2-butanedione in DMSO (80%)-*tert-*butyl alcohol (20%) containing excess potassium* tert-*butoxide; prepared by the reaction of a trace of oxygen with* n-*butyrophenone*

possible to describe uniquely their source. Among the most logical routes are:



Catalysis in the Oxidation of Phenones. Since autocatalysis or inhibition periods are not observed in phenone oxidations, it appears that the reaction is initiated by a direct reaction between the carbanion and molecular oxygen, a reaction of little importance in the oxidation of nitroalkanes or *p*-nitrotoluene derivatives.

$$RCOCHR^- + O_2 \rightarrow RCO\dot{C}HR + O_2\cdot^- \quad (21)$$

Among the possible routes to benzoic acid are the following:

$$C_6H_5COCHR^- + RO_2\cdot \rightarrow RO_2^- + C_6H_5CO\dot{C}HR \quad (22)$$

$$C_6H_5COCHR + O_2 \rightarrow C_6H_5COCHROO\cdot(RO_2\cdot) \quad (23)$$

$$C_6H_5COCHROO^- \rightarrow C_6H_5CO_2^- + RCHO \quad (24)$$

$$C_6H_5COCH(OOH)R \xrightarrow{B^-} C_6H_5COCOR \quad (25)$$

$$C_6H_5COCH(OOH)R + R^- \rightarrow 2\ C_6H_5COCH(OH)R\ (ROH) + RO^- \quad (26)$$

$$C_6H_5COCOR + C_6H_5COCH(OH)R \overset{-B}{\rightleftharpoons} 2\ [C_6H_5COCOR]\cdot^- \quad (27)$$

$$[C_6H_5COCOR]\cdot^- + O_2 \rightarrow C_6H_5COCOR + O_2\cdot^- \quad (28)$$

In cases where R contains an α-hydrogen atom the intermediate C_6H_5CO-COR can also be ionized to an enolate anion and oxidized to intermediates which ultimately yield benzoic acid.

Further evidence for a free-radical chain mechanism is provided by catalysis of phenone oxidation. Figure 15 shows considerable catalysis by nitrobenzene in the oxidation of acetophenone in *tert*-butyl alcohol solution containing potassium *tert*-butoxide. From Figure 15 it also appears that 0.2*M* acetophenone is completely ionized in *tert*-butyl alcohol at concentrations of potassium *tert*-butoxide greater than 0.4*M*. In the absence of oxygen, acidification of basic solutions of acetophenone under conditions where in the presence of oxygen oxidation would have been complete, yielded acetophenone in nearly quantitative yield. Thus, a base-catalyzed self-condensation of acetophenone is not important in the oxidation sequence.

Figure 16 illustrates the catalytic effects of a series of substituted nitroaromatics on the oxidation of acetophenone. The Hammett $\rho\sigma$ rela-

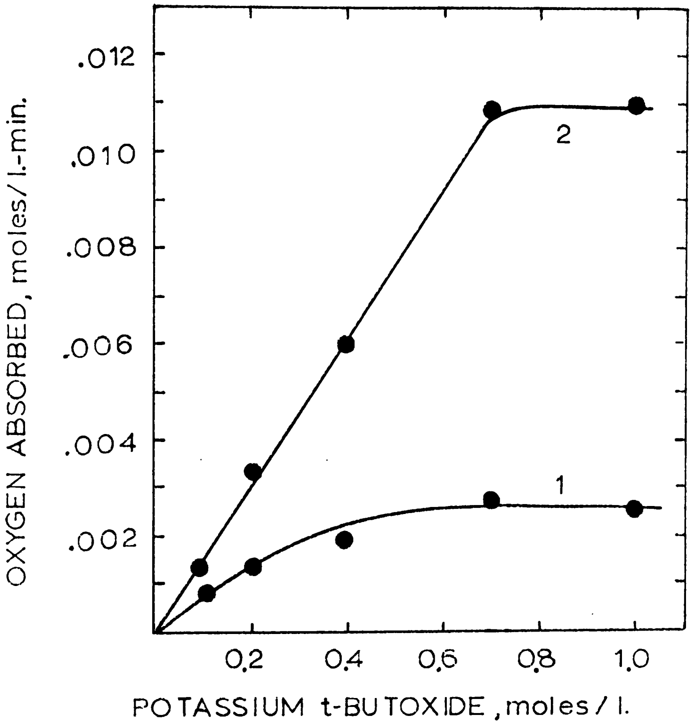


Figure 15. Oxidation of 0.2M acetophenone in tert-*butyl alcohol in the presence of potassium* tert-*butoxide. (1) no additive; (2) 0.12M nitrobenzene*

tionship is similar to that found in the oxidation of fluorene. Table XII summarizes the initial rates (by ESR) of electron transfer between acetophenone or propiophenone and substituted nitrobenzenes together with the observed rates of catalyzed oxidation of acetophenone. Again, as in the similar studies involving fluorene, there is a good correlation between the catalytic effects in oxidation and the rates of electron transfer in the absence of oxygen. Nitroaromatics are, however, not as efficient as catalysts in the oxidation of propiophenone as they are for acetophenone. This probably reflects differences in the oxidation rates of 1°- and 2°-enolate anions (*80*).

$$1°\text{-enolate anion} \begin{cases} \xrightarrow{O_2} 1°\text{-R}\cdot + O_2\cdot^- \text{ (slow)} \\ \xrightarrow{C_6H_5NO_2} 1°\text{-R}\cdot + C_6H_5NO_2\cdot^- \text{ (fast)} \end{cases}$$

$$2°\text{-enolate anion} \begin{cases} \xrightarrow{O_2} 2°\text{-R}\cdot + O_2\cdot \text{ (fast)} \\ \xrightarrow{C_6H_5NO_2} 2°\text{-R}\cdot + C_6H_5NO_2\cdot^- \text{ (fast)} \end{cases}$$

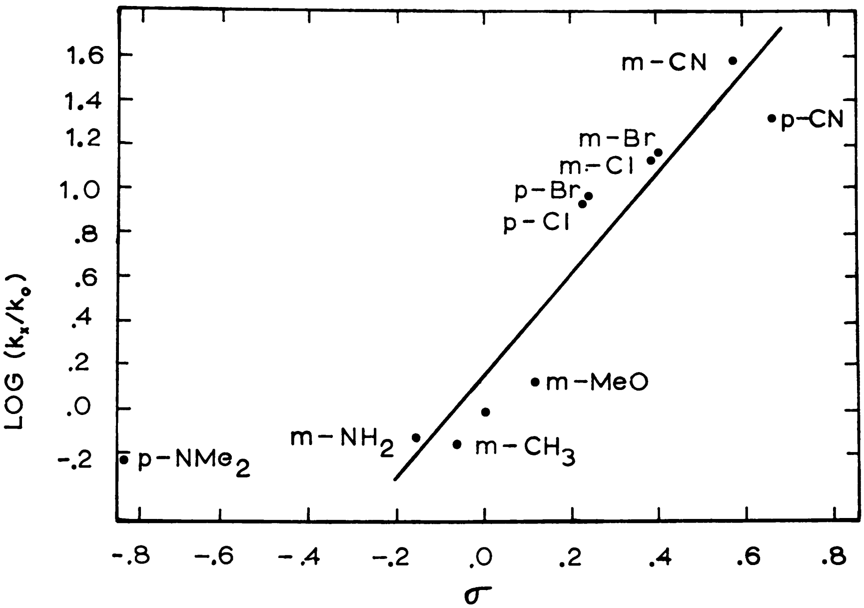


*Figure 16. Oxidation of 0.2*M *acetophenone in* tert-*butyl alcohol containing 0.4*M *potassium* tert-*butoxide and catalyzed by 0.1*M *nitrobenzenes,* k_0 *= rate catalyzed by nitrobenzene,* k_x *= rates catalyzed by substituted nitrobenzenes;* $\rho = 2.3$*;* m-*cyano,* p-*cyano,* p-*dimethylamino, and* p-*bromonitrobenzene were not completely soluble under the reaction conditions*

Table XII. Rates of Catalyzed Oxidation Transfer from Enolate Anions to

R =	Initial rate of oxidation of acetophenone in tert-BuOH, (mole oxygen/mole acetophenone/min.)	Electron transfer from acetophenone in tert-BuOH: Initial rate, moles/liter-min.	Electron transfer from acetophenone in tert-BuOH: Max. concn. of $RC_6H_4NO_2\cdot^-$, moles/liter
No catalyst	0.006		
p-$(CH_3)_2N$	0.012	0.000037	0.00002
m-CH_3	0.015	0.0013	0.0016
m-NH_2	0.016	0.0010	0.0025
H	0.021	0.0030	0.0016
o-I	0.022		
o-Br	0.025		
o-Cl	0.026		
m-CH_3O	0.029	0.0055	0.0061
p-Cl	0.191	0.038	0.023
p-Br	0.197		
m-Cl	0.308	0.043	0.023
m-Br	0.323		
p-CN	0.454		
m-CN	0.837		

[a] 0.2*M* Acetophenone, 0.1*M* propiophenone, 0.4*M* potassium *tert*-butoxide and 0.1*M* $RC_6H_4NO_2$ in *tert*-butyl alcohol solution; 0.2*M* potassium *tert*-butoxide and 0.005*M* $RC_6H_4NO_2$ in DMSO (80%) –*tert* butyl-alcohol (20%) solution.

An approximate estimate of kinetic chain length can be obtained from the data of Table XII. Thus, 0.1*M* nitrobenzene increased the initial oxidation rate of acetophenone from 0.0012 to 0.0040 moles oxygen absorbed/liter-min., $\Delta R_{O_2} = 0.0028$. Under the reaction conditions the rate of electron transfer to nitrobenzene in the absence of oxygen was measured as 0.003 moles/liter-min. Thus, one electron transfer reaction resulted in the consumption of only one molecule of oxygen. In the presence of nitroaromatics it appears that the initial oxidation process is best described as

$$RCOCH_2R \overset{B^-}{\rightleftharpoons} (RCOCHR)^-$$

$$(RCOCHR)^- + ArNO_2 \rightarrow RCO\dot{C}HR + ArNO_2\cdot^-$$

$$RCO\dot{C}HR + O_2 \rightarrow RCOCH(OO\cdot)R$$

$$RCOCH(OO\cdot)R + ArNO_2\cdot^- \xrightarrow{H^+} ArNO_2 + RCOCH(OOH)R$$

Effect of Structure on the Oxidation of Nitroalkanes and Phenones in Basic Solution. Table XIII illustrates that the rates of oxidation of nitrocarbanions and enolate anions in general follow the sequence 3° > 2° > 1° (*80*). This presumably reflects the stability of radicals 3° > 2° > 1°. This stability is reflected in the initiation steps of Reactions 17, 18, and 21 as well as in the main propagation reaction:

$$R:^- + ROO\cdot \rightarrow R\cdot + ROO:^-$$

of Acetophenone and Rates of Electron Substituted Nitroaromatics ($RC_6H_4NO_2$)[a]

Electron transfer from propiophenone in DMSO(80)-tert-BuOH(20)	
Initial rate, moles/liter-min.	*Max. conc. of $RC_6H_5NO_2\cdot^-$, moles/liter*
0.000015	0.00008
0.000003	
0.000041	0.00009
0.000063	0.00018
0.000030	0.00012
very fast	radical unstable

[b] *m*-Cyano, *p*-cyano, *p*-dimethylamino, and *p*-bromonitrobenzene were not completely soluble under the reaction conditions in *tert*-butyl alcohol.

Table XIII. Initial Rates of Oxidation of Nitroalkanes and Alkylphenones in Basic Solution[a]

Substrate, Moles/Liter	*Initial Rate of Oxidation, Moles/Liter-Min.*	*Total Oxygen Absorbed Mole/Mole Substrate*
CH_3NO_2 (0.60)	0.0009	1.6[b]
$CH_3CH_2NO_2$ (0.60)	0.004	1.5[b]
$(CH_3)_2CHNO_2$ (0.60)	0.010	1.8[b]
CH_3NO_2 (0.10)	0.0007	1.0
$CH_3CH_2NO_2$ (0.10)	0.004	1.5
$(CH_3)_2CHNO_2$ (0.10)	0.004	2.0
$C_6H_5COCH_3$ (0.60)	0.006	1.1[b]
$C_6H_5COCH_2CH_3$ (0.60)	0.040	1.3[b]
$C_6H_5COCH(CH_3)_2$ (0.60)	0.047	1.6[b]
$C_6H_5COCH_3$ (0.10)	0.014	1.7
$C_6H_5COCH_2CH_3$ (0.10)	0.014	1.3
$C_6H_5COCH(CH_3)_2$ (0.10)	0.006	1.0
$C_6H_5COCH_2C_6H_5$ (0.10)	0.005	2.0
$C_6H_5COCH_2C_6H_5$ (0.60)	0.005	1.8[b]

[a] DMSO (80%)-*tert*-butyl alcohol (20%) containing 0.224*M* potassium *tert*-butoxide.
[b] Mole oxygen absorbed per mole of base.

Some General Correlations

Our studies on the oxygenation of a number of carbanions of various structural types has in all cases led to the conclusion that oxidation involves a radical mechanism involving electron transfer from the carbanion to some electron acceptor. The reactivity of the carbanion in this electron transfer process accounts for most of the facts observed in the oxidations since both the initiation and propagation reactions are postulated to involve similar electron transfer processes.

In oxidative processes it is instructive to group carbanions into four categories:

(1) At one extreme we have the carbanions from weakly acidic hydrocarbons such as diphenylmethane and triphenylmethane. Here the rate of the initiation and propagation reactions are very fast, catalysis by an added electron acceptor such as nitrobenzene is of small magnitude, and the overall rate of oxidation is controlled mainly—or under some circumstances completely—by the rate of ionization of the parent hydrocarbon.

(2) More acidic substances such as the fluorenes or the alkyl phenones give carbanions more stable to oxygen since factors which stabilize carbanions need not be important in the stabilization of the corresponding radicals. For fluorenes and the alkylphenones a direct initiation reaction with oxygen appears to occur, but this reaction and the ensuing propagation reactions do not appear to be overwhelmingly fast compared to the rate of ionization of the substrate. Under these conditions large catalytic effects can be noted by adding electron acceptors, such as nitrobenzene, which are more efficient electron acceptors than molecular oxygen. In the absence of an added catalyst the initiation reaction with molecular oxygen is usually fast enough that autocatalysis of the autoxidation (by chain-branching reactions involving intermediate hydroperoxides) is not significant.

(3) Carbanions conjugated with a nitro group deserve consideration as a special category. The anions themselves are highly resonance stabilized, whereas there is little evidence that the nitro group gives any special stabilization to the corresponding radical. Many of these anions, e.g., 2-nitro-2-propyl, or tris(*p*-nitrophenyl)methyl, are in general stable to molecular oxygen at room temperature but can be made to undergo a catalyzed radical chain oxidation involving electron transfer from the carbanion to the peroxy radical. Some complexity is now introduced into the oxidation mechanism since the nitro substituent is itself an excellent one-electron acceptor and unionized nitroaromatics and, to a lesser extent the nitroalkanes, can catalyze a chain oxidation of their carbanions. The same type of spontaneous initiation reaction is observed for 1-phenylpropane-1,2-dione, methylanthraquinones, and *p*-phenylazotoluene. Now we find that the oxidation rates pass through maxima as the concentration of base (i.e., the percent ionization of the substrate) is increased. In the absence of any added catalyst, autocatalysis (involving intermediate hydroperoxides) may be observed because the spontaneous initiation process is slow. Moreover, if this chain-branching reaction can be eliminated, drastic inhibition is observable. Additional catalysis by electron acceptors, such as *m*-dinitrobenzene, is also readily observed. The simple *p*-alkylnitrobenzenes represent extreme cases of spontaneous initiation. Here the combination of the ionization rate of the *p*-nitrotoluene derivative and the one-electron accepting ability of the unionized *p*-nitroalkylaromatic are such that by choosing solvent and base, it is possible to achieve conditions wherein the ionization is immediately followed by electron transfer, and the rate of ionization can be measured by following the formation of the *p*-nitroalkylaromatic radical-anions by ESR spectroscopy (*62*).

(4) A fourth class of carbanions can be listed as those which do not undergo an initiation reaction with molecular oxygen and which are not even susceptible to electron transfer with an independently generated peroxy radical. Thus, a radical chain oxidation cannot be initiated, and even the possible initiation reactions with added catalysts (such as nitrobenzene) may be quite slow. Carbanions which fit into this class usually have two or more powerful anion-stabilizing groups conjugated with the carbanions. Among carbanions that appear to fit into this latter category are those derived from 2,2′,4,4′-tetranitrodiphenylmethane (slowly oxidized), *p*-nitrophenylacetonitrile (slowly oxidized), dibenzoylmethane, diethyl malonate, diethyl phenylmalonate, α-nitroacetophenone, α-cyanodeoxybenzoin, phenylnitromethane, 2-nitroindandione, 1,3-indanedione, 2-phenyl-1,3-indandione, acetylacetone, ethyl acetoacetate and 2,4,6-trinitrotoluene (slowly oxidized).

Dehydrogenations of Hydrocarbons and Derivatives in Basic Solution

We have examined intermolecular dehydrogenations of substituted toluenes and anilines by oxygen in basic solution, (*62, 65*):

$$p\text{-}NO_2C_6H_4CH_3 \xrightarrow[tert\text{-}BuOH]{B^-, O_2} p\text{-}NO_2C_6H_4CH_2CH_2C_6H_4NO_2\text{-}p$$

$$p\text{-}X\text{—}C_6H_4CH_3 \xrightarrow[DMSO(80\%)\text{-}tert\text{-}BuOH(20\%)]{B^-, O_2} p\text{-}X\text{—}C_6H_4CH{=}CHC_6H_4\text{—}X\text{-}p$$

$$C_6H_5NH_2 \xrightarrow[\text{DMSO(80\%)-}tert\text{-BuOH(20\%)}]{B^-,\ O_2} C_6H_4N{=}NC_6H_4$$

as well as the intramolecular oxidative dehydrogenation of a series of polyarylethanes and diarylketones.

$$ArCH_2{-}CH_2Ar \xrightarrow[\text{DMSO(80\%)-}tert\text{-BuOH(20\%)}]{B^-,\ O_2} ArCH{=}CHAr + O_2^{-2} + O_2\cdot^-$$

$$Ar_2CHOH \xrightarrow{B^-,\ O_2} Ar_2CO + O_2^{-2} + O_2\cdot^-$$

Oxidation of Substituted Toluenes and Anilines. The oxidation of *p*-nitrotoluene in the presence of alcoholic potassium hydroxide is a well known process (*62, 68*). The reaction forms *p,p'*-dinitrobibenzyl under mild conditions and *p,p'*-dinitrostilbene under more vigorous conditions. Both the bibenzyl and stilbene are rather insoluble in alcohols. In DMSO(80%)–*tert*-butyl alcohol(20%) solution *p*-nitrotoluene is rapidly converted by oxygen to *p*-nitrobenzoic acid. The bibenzyl and stilbene are soluble in this solvent and oxidation apparently involves

$$p\text{-}NO_2C_6H_4CH_3 \xrightarrow[O_2]{B^-} p\text{-}NO_2C_6H_4CH_2CH_2C_6H_4{-}NO_2\text{-}p \xrightarrow[O_2]{B^-}$$

$$p\text{-}NO_2{-}C_6H_4CH{=}CHC_6H_4{-}NO_2\text{-}p \xrightarrow[O_2]{B^-} p\text{-}NO_2C_6H_4CO_2^-$$

Other derivatives of *p*-nitrotoluene which ionize to form a 2°- or 3°-carbanion give normal oxygenation products, e.g.,

$$p\text{-}NO_2C_6H_5CH_2CH_3 \xrightarrow[O_2]{B^-} p\text{-}NO_2C_6H_4CO_2H$$

$$p\text{-}NO_2C_6H_4CH(CH_3)_2 \xrightarrow[O_2]{B^-} p\text{-}NO_2C_6H_4C(CH_3)_2OH$$

$$p\text{-}NO_2C_6H_4CH_2C_6H_5 \xrightarrow[O_2]{B^-} p\text{-}NO_2C_6H_4COC_6H_5$$

The coupling reaction of *p*-nitrotoluene is atypical of other oxidations of substituted toluenes. The coupling reaction occurs in the absence of oxygen with the formation of *p*-nitrotoluene radical-anion (*62*).

$$p\text{-}NO_2C_6H_4CH_3 \rightarrow p\text{-}NO_2C_6H_4CH_2^-$$

$$p\text{-}NO_2C_6H_5CH_2^- + p\text{-}NO_2C_6H_4CH_3 \rightarrow [\text{complex}]^-$$

$$[\text{complex}]^- + 2\,p\text{-}NO_2C_6H_4CH_3 \rightarrow p\text{-}NO_2C_6H_4CH_2CH_2C_6H_4NO_2\text{-}p + 2\,p\text{-}CH_3C_6H_4NO_2\cdot^- + H_4$$

The initial rate of formation of *p,p'*-dinitrobibenzyl is approximately the same in the presence and absence of oxygen so that the only effect of oxygen in the oxidation process is to regenerate *p*-nitrotoluene:

$$p\text{-}CH_3C_6H_4NO_2\cdot^- + O_2 \rightarrow p\text{-}CH_3C_6H_4NO_2 + O_2\cdot^-$$

and at high oxygen pressures or low *p*-nitrotoluene concentrations, to

convert some of the *p*-nitrobenzyl anions to *p*-nitrobenzoic acid. The spontaneous oxidation-reduction process leading to the dimer and radical-anion in the absence of oxygen is a fairly widespread reaction having been noted for aminoanthraquinones (*28*, *30*) and 4-nitro-3-picoline-*N*-oxide (*72*).

Although toluene itself cannot be readily oxidized via the intervention of a carbanion intermediate, the methylnaphthalenes or methylpyridines are readily converted to the carboxylic acids in DMSO(80%)–*tert*-butyl alcohol(20%) or hexamethylphosphoramide solution or at a slightly elevated temperature in DMF–*tert*-butyl alcohol solutions (*85*). It has been recently reported that toluene is oxidized to benzoic acid at 100° C. in diphenyl sulfoxide solution containing a large excess of mostly insoluble potassium *tert*-butoxide (*81*). It was also suggested that the benzyl anion was an intermediate in this process. Our own studies of the hydrogen-deuterium exchange of α-d_1-toluene under the reaction conditions has shown that the benzyl anion may well be an intermediate in this process with the rate of oxidation being approximately equal to the rate of exchange.

A variety of substituted toluenes (p-X–$C_6H_4CH_3$) wherein X = C_6H_5CO–, NC–, $CH_3C_6H_5CO$–, $C_6H_5SO_2$–, p-$CH_3C_6H_4SO_2$–, p-C_6H_4-N=N–, and CH_3O_2C–, are oxidized to a mixture of the corresponding stilbene dimer and acid.

$$\text{-}C_6H_5SO_2C_6H_4CH_3 \xrightarrow[\text{DMSO (80\%)-}tert\text{-BuOH(20\%)}]{B^-,\ O_2} C_6H_5SO_2C_6H_4CH{=}CHC_6H_4SO_2C_6H_5 + p\text{-}C_6H_5SO_2C_6H_4CO_2H$$

In the case of X = p-$CH_3C_6H_4CO$– and p-$CH_3C_6H_4SO_2$– the product is a low molecular weight polystilbene with carboxyl end groups (Y = >CO, >SO_2)

$$HO_2CC_6H_4\text{-}(Y{=}C_6H_4CH{=}CHC_6H_4)_n\text{-}Y\text{—}C_6H_4CO_2H$$

No trace of the saturated dimers was found. In addition the ratio of acid to stilbene was not particularly sensitive to the concentrations of the reactants. These results appear to rule out the stilbene formation as involving

$$p\text{-}XC_6H_4CH_3 \xrightarrow[O_2]{B^-} p\text{-}XC_6H_4CH_2\cdot \rightarrow p\text{-}XC_6H_4CH_2\text{—}CH_2C_6H_4X\text{-}p \xrightarrow[O_2]{B^-} p\text{-}XC_6H_4CH{=}CHC_6H_4X\text{-}p$$

The stilbenes can be formed by condensation of the aldehyde and toluene derivative in DMSO(80%)–*tert*-butyl alcohol(20%) in the presence of potassium *tert*-butoxide (*11*).

$$p\text{-}XC_6H_4CHO + p\text{-}XC_6H_4CH_3 \rightarrow p\text{-}XC_6H_4CH{=}CHC_6H_4X\text{-}p$$

Similarly, nitrosobenzene and aniline condense to form azobenzene.

$$C_6H_5NO + C_6H_5NH_2 \xrightarrow{B^-} C_6H_5N{=}NC_6H_5$$

Final conformation of an oxidation mechanism involving condensation to form azobenzene and stilbene derivatives was obtained by using C^{14}-labeled nitrosobenzene and *p*-(phenylsulfonyl)benzaldehyde. Slowly adding radioactive nitrosobenzene to aniline being oxidized in DMSO-(80%)–*tert*-butyl alcohol(20%) containing potassium *tert*-butoxide indicated that under the oxidation conditions, the nitrosobenzene was converted to azobenzene in a yield approximately equal to the overall yield of azobenzene from aniline. Similarly, adding about 5% (based on phenyl-*p*-tolylsulfone) of C^{14} labeled *p*-(phenylsulfonyl)benzaldehyde to an oxidation of phenyl-*p*-tolylsulfone indicated that radioactive aldehyde was converted to *p*-(phenylsulfonyl)benzoic acid and *p,p'*-di(*p*-phenylsulfonyl(stilbene in the same ratio as phenyl-*p*-tolylsulfone was converted to the acid and stilbene. The oxidation of substituted toluenes thus follows the course:

$$p\text{-}XC_6H_4CH_3 \xrightarrow[O_2]{B^-} p\text{-}XC_6H_4CHO \begin{cases} \xrightarrow{O_2} p\text{-}XC_6H_4CO_2H \\ \xrightarrow{p\text{-}XC_6H_4CH_2^-} p\text{-}XC_6H_4CH{=}CHC_6H_4X\text{-}p \end{cases}$$

Oxidative Dehydrogenation of 1,2-Diarylethanes and Dihydroaromatics. The oxidations of a series of aryl-substituted ethanes and dihydro derivatives of polycyclic aromatic compounds are summarized in Table XIV. Bibenzyl did not undergo oxidation under the reaction conditions in either DMSO or HMPA.

Table XIV. Oxidation of Polyarylethanes and Dihydroaromatics at 25°C. ± 2°[a]

Substrate	*Initial Rate*[b]	*Oxygen Absorbed*[c]	*Product Isolated(Yield)*
Tetraphenylethane[d]	0.03	1.0	tetraphenylethylene (96%)
1,2-Bis(4-pyridyl)ethane	1.1	3.0	
1,2-Bis(2-pyridyl)ethane	0.3	1.9	
Acenaphthene	0.25	4.0	naphthalic anhydride (63%)[f]
Acenaphthene[e]	1.6		
9,10-Dihydrophenanthrene	0.05		
9,10-Dihydrophenanthrene[e]	0.6	2.4	phenanthrene (88%)
1,2-Dihydropyrene	0.12	1.9	
1,2-Dihydropyrene[e]	1.0	2.1	pyrene (90%)
Acridan	2.5	1.9	acridine (87%)
9,10-Dihydroanthracene	3.5	1.9	anthracene (69%); anthraquinone (11%); anthraquinone-DMSO adduct (10%)

[a] 0.1*M* substrate, 0.5*M* potassium *tert*-butoxide in 40 ml. of DMSO (80%)-*tert*-butyl alcohol (20%).
[b] Moles oxygen/mole substrate per min.
[c] Moles/mole of substrate at complete oxidation.
[d] Heterogeneous.
[e] Hexamethylphosphoramide.
[f] An oxidation of acenaphthene halted after the absorption of one mole of oxygen yielded naphtha anhydride (10%) and unreacted acenaphthene (60%); acenaphthylene did not oxidize under the reaction conditions.

The substances investigated oxidized in every case (except for acenaphthene) to give the parent unsaturated compound with an oxygen stoichiometry of usually 2 moles of oxygen per mole of hydrocarbon and with the formation of potassium superoxide.

$$R_2CH—CHR_2 + 2\ KOR' + 2\ O_2 \rightarrow R_2C{=}CR_2 + 2\ R'OH + 2\ KO_2$$

A number of 1,2-diphenylethane derivatives and dihydroaromatics produce radical-anions when exposed to small amounts of oxygen in DMSO–*tert*-butyl alcohol solutions containing potassium *tert*-butoxide. Detecting paramagnetic substances in low concentrations during these oxidations does not demand that the paramagnetic substance is a key intermediate in the oxidation reaction. In fact, the radical-anion may simply represent a reaction by-product. However, detecting paramagnetic substances is consistent with a radical type of oxidation.

The oxidation of 9,10-dihydroanthracene in DMSO(80%)–*tert*-butyl alcohol(20%) produced the anthrasemiquinone radical-anion whose spectrum was similar to that reported in pure DMSO (*78*). Under the same conditions 9,10-dihydrophenanthrene also gave the semiquinone. The spectrum could not be completely resolved but was similar to a published spectrum (*21*).

A solution of acridan in dimethyl sulfoxide(80%)–*tert*-butyl alcohol-(20%) containing 0.22*M* potassium *tert*-butoxide turned green on exposure to oxygen and gave the spectrum shown in Figure 17. Since the

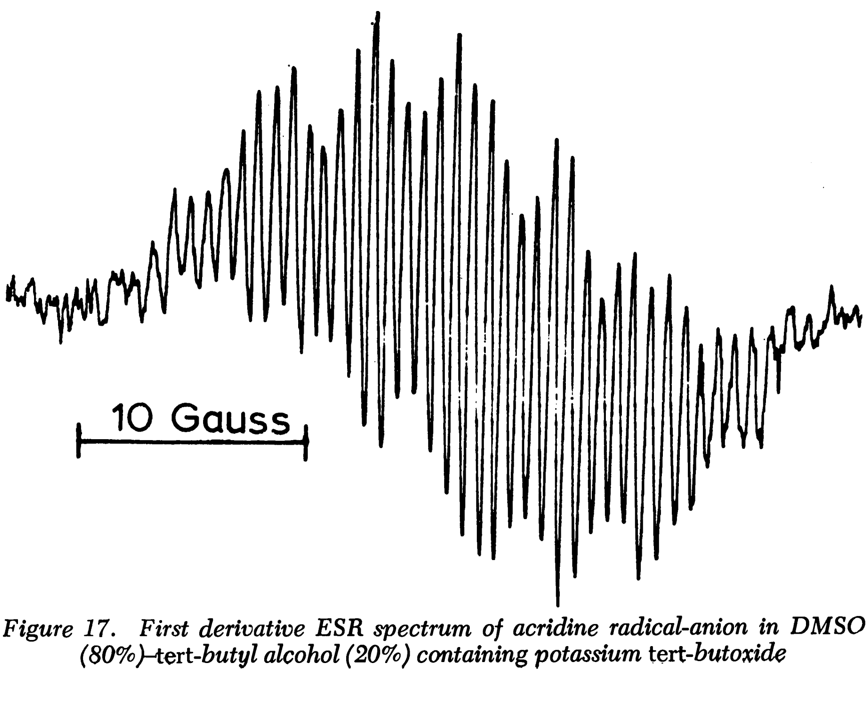


*Figure 17. First derivative ESR spectrum of acridine radical-anion in DMSO (80%)–*tert*-butyl alcohol (20%) containing potassium *tert*-butoxide*

same spectrum was obtained via electron transfer between acridine and acridan or from 9,9′-biacridanyl under similar conditions (*62, 63*), it was concluded that the acridine radical-anion was formed in the oxidation of acridan. No free-radical signal was obtained under similar conditions from the basic solutions of acridine exposed to air.

. In pure DMSO solutions containing 0.1–0.5*M* potassium *tert*-butoxide, high concentrations of paramagnetic substances were obtained by exposing 9,10-dihydroanthracene, acenaphthene, and 9,10-dihydrophenanthrene to oxygen. The brown solutions of the anions developed dark green, red purple, and red colors, respectively. These intermediates have been identified as the radical-anions derived from the parent unsaturated system. However, oxidations in the presence of *traces* of potassium *tert*-butoxide produced the semiquinones even in pure DMSO.

The aromatic radical-anions were produced by electron transfer between the anions derived from the dihydroaromatic with the parent aromatic hydrocarbon in the absence of oxygen. Figure 18 indicates the approximate extent of such transfer as a function of time. The extent of transfer,

$$ArH_2 + Ar \overset{B^-}{\rightleftharpoons} 2Ar^{\cdot -}$$

was essentially 100% for 9,10-dihydroanthracene–anthracene within 1 minute after mixing with base. Under the reaction conditions 1,2-dihydropyrene–pyrene did not give a radical signal. Dihydropyrene in the presence of potassium *tert*-butoxide in DMSO or HMPA solutions did not yield a paramagnetic intermediate in the presence of a trace of oxygen even though the solutions developed a pink coloration. Apparently the dianion is not as readily formed in this system as from dihydrophenanthrene.

When significant concentrations of the aromatic hydrocarbon radical-anions had been generated in pure DMSO from the reaction of traces of oxygen with basic solutions of the dihydroaromatics, further exposure of the solutions to traces of oxygen had little effect on the ESR spectra except that the intensity of the signal gradually decreased. Only when the concentration of aromatic hydrocarbon radical-anion had been reduced to a low value did additional oxygen cause the line width of the ESR signal to decrease and the spectrum gradually change to that of the semiquinone.

Carbanion oxidations in which intramolecular dehydrogenation occurs present a difficult mechanistic problem. The final step in the formation of the unsaturated compound from a radical-anion can be formulated as either reaction 29, 30, or 31.

$$>\dot{C}\text{—}X^- + O_2 \rightarrow \text{—}\overset{\overset{O\cdot}{|}}{\underset{|}{\overset{O}{|}}}{C}\text{—}X^- \rightarrow >C = X + O_2{\cdot}^- \qquad (29)$$

$$>\dot{C}{-}X^- + O_2 \rightarrow >C = X + O_2\cdot^- \quad (30)$$

$$>C(OO\cdot){-}X^- + R\!:^- \text{[or } O_2\cdot^-] \rightarrow R\cdot \text{ [or } O_2] + >C(OO^-){-}X^- \rightarrow >C = X + O_2^{-2} \quad (31)$$

In many cases Reaction 31 can be excluded by the formation of the superoxide anion [$O_2\cdot^-$] as the reaction product with an oxygen stoichiometry of 2 moles of oxygen absorbed per mole of dihydro compound. The formation of the superoxide anion as a reaction product is not noted in oxidations wherein the carbanion is converted to an oxygenated product via a peroxy radical pathway—e.g., polyarylmethanes, fluorene, or phenones—even though there is evidence that the initiation reaction involves electron transfer between the carbanion and oxygen.

$$R\!:^- + O_2 \rightarrow R\cdot + O_2\cdot^-$$

Apparently the superoxide is rapidly consumed in a chain termination step.

$$ROO\cdot + O_2\cdot^- \rightarrow ROO\!:^- + O_2$$

This conclusion is supported by the observation that although preformed potassium superoxide removes the induction period from the

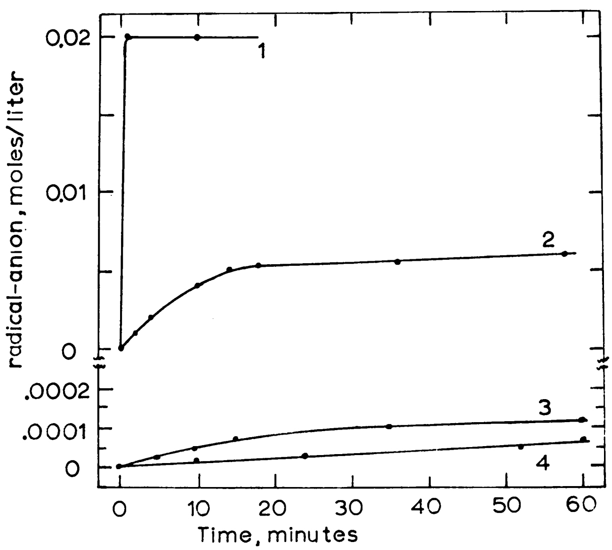
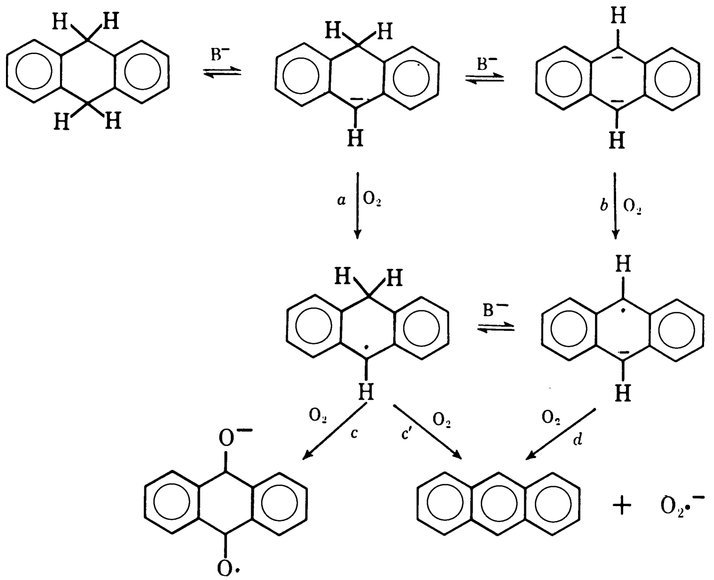


*Figure 18. Electron transfer between dihydroaromatic (0.01*M*) and aromatic hydrocarbons (0.01*M*) in dimethyl sulfoxide containing 0.1*M *potassium* tert-*butoxide: (1) anthracene-dihydroanthracene; (2) acenaphthylene-acenaphthene; (3) phenanthrene-9,10-dihydrophenanthrene, saturated (~0.5*M*) solution of base; (4) phenanthrene-9,10-dihydrophenanthrene*

oxidation of benzhydrol, it has the overall effect of reducing the maximum oxidation rate obtainable. We would thus like to suggest that the formation of superoxide anion as a reaction product is inconsistent with an oxidation sequence involving a peroxy radical (e.g., Reaction 29 or 31 except when the peroxy radical has only transitory stability).

The question of whether a given oxidation involves a mono- or a dianion, or both, is also a difficult subject to approach. The observation that exposing 9,10-dihydroanthracene, acenaphthene, or 9,10-dihydrophenanthrene to a trace of oxygen in DMSO(80%)–*tert*-butyl alcohol-(20%) produces only the semiquinone radical-anion whereas in pure DMSO the aromatic radical-anion was produced, suggests that the semiquinones are oxidation products of monoanions (oxidation path *a*) while the aromatic radical-anions are intermediates in the oxidation of dianions (path *b–d*).



Oxidation of Diarylcarbinols in Basic Solution. The autoxidation in basic solution of benzyl alcohols to benzoic acids and benzhydrols to benzophenones is well known (*7, 24, 26, 27, 37, 48, 49*). LeBerre has commented on possible mechanisms for these autoxidations and particularly for the oxidation of benzhydrol (*27, 48, 49*). He concluded that oxidizing suspensions of the sodium or potassium salts of benzhydrol in benzene or tetrahydrofuran involved dianions as intermediates and was possibly a free radical chain process (*27, 49*).

$$2\ R_2CHO^- \rightarrow R_2CHOH + R_2CO^{-2}$$

$$R_2CO^{-2} + O_2 \rightarrow R_2CO\cdot^- + O_2\cdot^-$$

$$R_2CO\cdot^- + O_2 \rightarrow R_2C(O^-)OO\cdot$$

The possibility that the reaction involved attack on the α-hydrogen atom was considered,

$$R_2C(O^-)OO\cdot + R_2CHO^- \rightarrow R_2C(O^-)OOH + R_2CO\cdot^-$$

in addition to various propagation steps involving the dianion (27, 49).

$$R_2CO^{-2} + O_2\cdot^- \rightarrow R_2CO\cdot^- + O_2^{-2}$$

$$R_2CO^{-2} + R_2C(O^-)OO\cdot \rightarrow R_2CO\cdot^- + R_2C(O^-)OO^-$$

LeBerre observed in the presence of excess sodium or potassium *tert*-butoxide that the oxygen was converted to the superoxide rather than to the peroxides (MOOH, MOOM) observed with stoichiometric amounts of base (48, 49). This was explained by an unusual reaction, the further oxidation of the peroxide to the superoxide

$$M_2O_2 + O_2 \xrightarrow[\text{or } C_6H_5CH_3]{\text{THF}, C_6H_6} 2\ MO_2$$

We have studied the oxidation of a number of benzylic alcohols in the presence of alkoxide ions under homogeneous conditions by the use of *tert*-butyl alcohol, pyridine or dimethyl sulfoxide as solvent. We have been particularly interested in obtaining evidence for or against the participation of a carbanion or a dianion in the oxidation since the formation of $(C_6H_5)_2COH^{-1}$ or $(C_6H_5)_2CO^{-2}$ by the action of alkoxide ion appeared to us to be expected. Our results are not consistent with the intervention of a carbanion in the oxidation of benzhydrol or benzyl alcohols but do suggest carbanion or dianion formation in the oxidation of the more acidic 9-xanthenol, 9-fluorenol, and *p*-nitrobenzyl alcohol.

In solvents where the base and diarylcarbinol are soluble we have observed that the ratio of superoxide to alkali metal peroxide formed at complete oxidation depends on the alkali metal involved, the concentration of base, the solvent, and the structure of the carbinol. The effect of the carbinol structure argues against the formation of the superoxide solely from further oxidation of the alkali metal peroxide; the yield of the superoxide appears to be determined by its solubility characteristics and the reactivity of the alcohol being oxidized.

Table XV summarizes a number of oxidations of benzhydrol in the presence of bases and a number of potential catalysts or inhibitors.

The lack of significant solvent effects as well as the lack of a significant effect of excess base concentration on the oxidation rates of benzhydrol appear to exclude an oxidation mechanism involving $(C_6H_5)_2COH^{-1}$ or $(C_6H_5)_2CO^{-2}$ under the conditions employed. Significant effects of these variables were found in the oxidation of fluorene and triphenylmethane in basic solution—reactions recognized to proceed via carbanion intermediates. Additional evidence for the lack of carbanion or dianion intermediates is the fact that the rate differences between benzhydrol and α-deuteriobenzhydrol are too large (25-fold in *tert*-butyl alcohol solution)

Table XV. Oxidations of Benzhydrol

Conc. of Benzhydrol, Moles/Liter	*Conc. of $KOC(CH_3)_3$, Moles/Liter*	*Added Substance, Moles/Liter*
0.10	0.00	—
0.06	0.18	—
0.12	0.12	—
0.12	0.24	—
0.12	0.36	—
0.12	0.48	—
0.12[b]	0.36	—
0.12	0.36	As_2O_3 (0.01)
0.10	0.22	$C_6H_5NO_2$ (0.01)
0.10	0.22	$(C_6H_5)_2CO$ (0.01)
0.15	0.39	$FeCl_3$ (0.002)
0.15	0.39	$Cu(OAc)_2 \cdot H_2O$ (0.002)
0.16	0.34	$CuSO_4$ (0.002)
0.16	0.39	$CuCl_2$ (0.002)

[a] Moles oxygen/mole benzhydrol/min., maximum rate observed, often after an induction period (see Figure 19).

for a simple isotope effect in an ionization process. Furthermore, under the reaction conditions of line 7 in Table XV, α-deuteriobenzhydrol did not undergo exchange to form benzhydrol during a 24-hour period (analysis by NMR). Unreacted alcohol recovered from the oxidation of α-deuteriobenzhydrol in DMSO(80%)–*tert*-butyl alcohol(20%) solution showed no benzylic protons even after an oxidation period of 6 hours.

The reaction of benzhydrol and benzophenone in *tert*-butyl alcohol or DMSO(80%)–*tert*-butyl alcohol(20%) solutions containing excess base does not yield appreciable quantities of benzophenone ketyl readily detected by ESR spectroscopy presumably because of the absence of the dianion derived from the benzhydrol. In a typical experiment only 0.004% of the starting benzhydrol and benzophenone was converted to the ketyl. Reaction of traces of oxygen with benzhydrol in the presence of excess potassium *tert*-butoxide did give significant concentrations of the ketyl in pure DMSO solution but not in *tert*-butyl alcohol or DMSO-(80%)–*tert*-butyl alcohol(20%) solutions. This is consistent with the presence of the dianion in DMSO but not in the other solvents.

$$(C_6H_5)_2CHOH \underset{\text{DMSO}}{\overset{\text{base}}{\rightleftharpoons}} (C_6H_5)_2CO^{-2}$$

$$(C_6H_5)_2CO^{-2} + (C_6H_5)_2CO \rightleftharpoons 2\,(C_6H_5)_2CO\cdot^{-}$$

That the ketyl is stable in DMSO(80%)–*tert*-butyl alcohol(20%) was demonstrated by the rapid formation of significant amounts of the ketyl from benzpinacol in this solvent in the presence of excess potassium *tert*-butoxide, but with absence of air. The benzophenone ketyl is also gen-

in Basic Solutions at 25°C. ± 2°

Rates of Oxygen Absorption[a]		
Dimethyl Sulfoxide(80%)–tert-Butyl Alcohol (20%)	*Pyridine(80%) tert-Butyl Alcohol (20%)*	*tert-Butyl Alcohol*
0.00	0.00	0.00
0.012	0.009	0.012
—	—	0.005
0.010	0.017	0.015
0.016	—	0.019
—	—	0.023
0.0015	—	0.0007
—	—	0.017[c]
—	0.018	—
—	0.015	—
—	—	0.001
—	—	0.020[d]
		0.007[d]
		0.015[d]

[b] α-Deuteriobenzhydrol.
[c] After a pronounced induction period of 4 hrs. during which rate was 0.0001.
[d] No induction period.

erated from benzpinacol in ethanol containing sodium ethoxide and pyridine containing lithium *tert*-butoxide. These observations demand that the source of the ketyl from the pinacol in DMSO–*tert*-butyl alcohol solutions is via path *e* rather than via path *f*.

$$Ar_2C(OH){-}C(OH)Ar_2 \overset{base}{\rightleftharpoons} Ar_2(O^-){-}C(O^-)Ar_2 \overset{e}{\rightleftharpoons} 2\ Ar_2\dot{C}{-}O^-$$

$$Ar_2(O^-){-}C(O^-)Ar_2 \rightleftharpoons Ar_2CO + Ar_2CO^{-2} \overset{f}{\longrightarrow} Ar_2\dot{C}{-}O^-$$

Figure 19 shows that the oxidation of benzhydrol in *tert*-butyl alcohol solution is autocatalytic and is inhibited by ferric salts or arsenic trioxide. Catalysis by nitroaromatics, characteristic of the oxidation of the carbanions derived from fluorene, the nitroalkanes, and the alkylphenones, was not observed.

All the above observations point to a free-radical chain oxidation not involving a carbanion or dianion. The ease of initiation and propagation of the reaction presumably results from the ease of attack of a radical species on the α-hydrogen atom of the alcoholate anion.

$$X\cdot + (C_6H_5)_2CHO^- \rightarrow HX + (C_6H_5)_2CO\cdot^-$$

The bond dissociation energy of an alpha carbon–hydrogen bond in an alkoxide anion should be quite slow because of the stability of the resulting ketyl anion.

The stoichiometry of the reaction of oxygen with benzhydrol (Table XVI) varies with the concentration of base although the oxidation rates (Table XV) are relatively independent of the concentration of base. Benzophenone is formed in excellent yield (> 95%) in the presence of

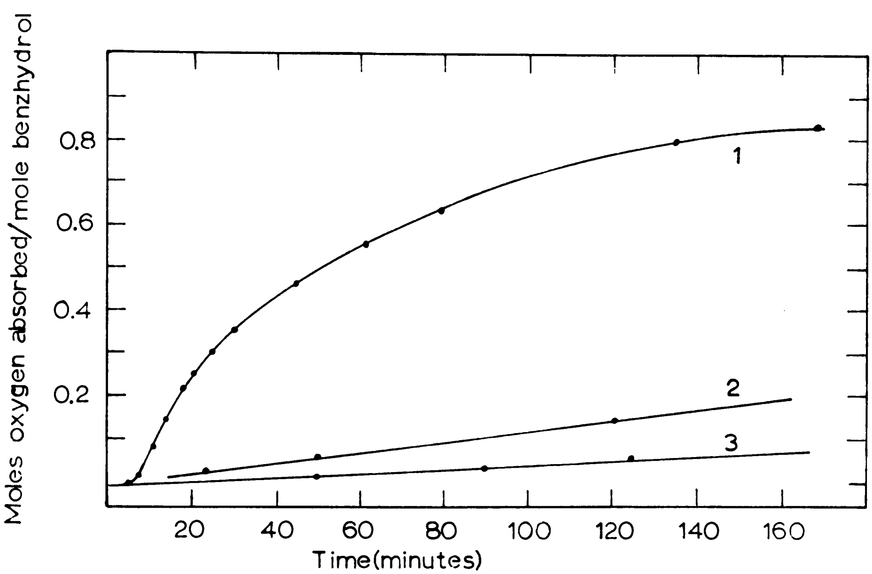


*Figure 19. Oxidation of 0.12*M *benzhydrol in* tert-*butyl alcohol containing 0.36*M *potassium* tert-*butoxide; (1) no additive; (2) 0.002*M *$FeCl_3$; (3) 0.01*M *As_2O_3*

excess base except in DMSO(80%)-*tert*-butyl alcohol(20%) solutions where the benzophenone-DMSO adduct is the major product. The variable stoichiometry of Table XVI results from the concurrent formation of potassium peroxide and superoxide (*48, 49*).

$$(C_6H_5)_2CHOH + O_2 + KOR \rightarrow (C_6H_5)_2CO + KO_2 + K_2O_2 + HOR$$

Table XVI. Oxygen Stoichiometry in the Oxidation of Benzhydrol[a]

Potassium tert-Butoxide, Moles/Liter	*Solvent*	*Moles Oxygen Absorbed per Mole Benzhydrol (minutes)*	*Recovered Benzhydrol, %*
0.12	*tert*-BuOH	0.73 (1100)	13
0.20	*tert*-BuOH	0.91 (625)	
0.24	*tert*-BuOH	1.02 (425)	7
		1.13 (1100)	
0.36	*tert*-BuOH	1.36 (1200)	3
0.48	*tert*-BuOH	1.45 (1400)	
		1.16 (1400)[b]	
0.24	DMSO(80%)-*tert*-BuOH(20%)	1.33 (600)[c]	0
0.36	DMSO(80%)-*tert*-BuOH(20%)	1.65 (275)	0

[a] 0.12*M* in benzhydrol.
[b] Oxidation was initially 0.20*M* in $KOC(CH_3)_3$. After 625 min., 0.91 moles of oxygen/mole of benzyhdrol had been absorbed. The base concentration was then increased to 0.48*M*.
[c] Product 75% benzophenone, 25% benzophenone-DMSO adduct.

Table XVI indicates that in the presence of a slight excess of base the reaction proceeds fairly cleanly to give potassium peroxide. In the presence of large excesses of potassium *tert*-butoxide the reaction gives

significant amounts of potassium superoxide which precipitates from the solution as a yellow powder.

Since the overall rate of oxidation is fairly independent of the amount of excess base (Table XV), it appears that the changing stoichiometry may reflect the formation of an insoluble complex between potassium superoxide and potassium *tert*-butoxide which stabilizes the superoxide against further reactions.

In the oxidation of 3 mmoles of benzhydrol [0.12*M*] in 25 ml. of 0.48*M* potassium *tert*-butoxide in *tert*-butyl alcohol solution, 4.35 mmoles of oxygen was absorbed at complete reaction, and a crude precipitate was formed which contained only 65% KO_2 as analyzed by the method of Seyb and Kleinberg (73). Thorough washing with *tert*-butyl alcohol gave 0.26 grams (3.6 mmoles) of potassium superoxide of 95% purity. The remaining 0.75 mmoles of oxygen was presumably present in the form of soluble potassium peroxides. In the oxidation of 0.12*M* benzhydrol in the presence of 0.36*M* potassium *tert*-butoxide is DMSO(80%)–*tert*-butyl alcohol(20%) solvent, 4.95 mmoles of oxygen were absorbed by 3 mmoles of benzhydrol at complete reaction. The precipitated superoxide after thorough washing with the reaction solvent weighed 0.307 grams (4.25 mmoles of superoxide) and analyzed as 103% potassium superoxide. In this case the experimental stoichiometry (277 minute reaction period) is indicated in the following equation (mmoles in parentheses).

$$(3.00)(C_6H_5)_2CHOH + (4.95)\ O_2 + (9.00)\ KOC(CH_3)_3 \rightarrow$$
$$(0.8)(C_6H_5)_2CO + (2.2)(C_6H_5)_2C(OH)CH_2SOCH_3 + (4.25)\ KO_2$$

The autocatalysis involved in the oxidation of benzhydrol appears to be connected with the formation and presence of potassium superoxide rather than benzophenone. The addition of potassium superoxide precipitated from a previous oxidation removes the autocatalysis while benzophenone has no effect. Arsenic trioxide and Fe(III) apparently destroy the superoxide and give rise to induction periods. The autocatalytic nature of the oxidation, the inhibition by Fe(III) and arsenic trioxide, and the large isotope effect observed are all consistent with extensive chain branching from reactions of potassium superoxide. At low concentrations of base where the autocatalysis is most pronounced and the product mainly potassium peroxide, the oxidation appears to be best explained by the following sequence of reactions.

$$(C_6H_5)_2CHO^- + O_2 \xrightarrow{\text{slow}} (C_6H_5)_2CO\cdot^- + O_2\cdot^- + H^+$$
$$(C_6H_5)_2CHO^- + O_2\cdot^- \rightarrow (C_6H_5)_2CO\cdot^- + O_2^{-2} + H^+$$
$$(C_6H_5)_2CO\cdot^- + O_2 \rightarrow (C_6H_5)_2CO + O_2\cdot^-$$
$$(C_6H_5)_2CO\cdot^- + O_2\cdot^- \rightarrow (C_6H_5)_2CO + O_2^{-2}$$

Pertinent rate data for the oxidation of 9-fluorenol and 9-xanthenol are summarized in Table XVII. Adding ferric salts accelerated the

Table XVII. Oxidation of Fluorenol and Xanthenol

Substrate, Moles/Liter	Base,[a] Moles/Liter	Added Substrate[b]	Initial Oxidation Rates[c] tert-BuOH	Pyridine (80%)	DMSO (80%)
Xanthenol, 0.12	0.36		0.10[d]		
Xanthenol, 0.06	0.18		0.06[d]	0.15	0.50
Fluorenol, 0.12	0.36		0.25[d]		
Fluorenol, 0.06	0.18		0.28	1.1	1.9
9-Deuteriofluorenol, 0.06	0.18				1.8
7-Acenaphthenol, 0.06	0.18			1.5	
Xanthenol, 0.06	0.18[e]				0.70[d]
Xanthenol, 0.06	0.18[f]				0.90[d]
Xanthenol, 0.06	0.18[g]				0.45
Xanthenol, 0.10	0.22			0.15	
Xanthenol, 0.10	0.22	$C_6H_5NO_2$		0.30	
Xanthenol, 0.10	0.22	*p*-$ClC_6H_4NO_2$		0.35	
Xanthenol, 0.10	0.22	*p*-$BrC_6H_4NO_2$		0.40	
Xanthenol, 0.10	0.22	*p*-$CNC_6H_4NO_2$		1.0	
Xanthenol, 0.10	0.22	4-nitropyridine-*N*-oxide		1.2	

[a] Potassium *tert*-butoxide unless otherwise specified.
[b] 0.005*M*.
[c] Moles oxygen/mole substrate/minute.
[d] Heterogeneous.
[e] Lithium *tert*-butoxide.
[f] Sodium *tert*-butoxide.
[g] Rubidium *tert*-butoxide.

oxidation rate of fluorenol and also changed the stoichiometry (Figure 20). The catalysis appears to involve electron transfer,

$$Ar_2CO^{-2} + Fe(III) \rightarrow Ar_2CO\cdot^{-} + Fe(II)$$

while the stoichiometry is consistent with an iron-catalyzed decomposition of potassium peroxide or superoxide.

$$KO_2;\ K_2O_2 \xrightarrow{Fe} K_2O + O_2$$

The catalysis by nitroaromatics of the oxidation of xanthenol (Figure 21) and the pronounced effect of solvents on the rates of oxidation of xanthenol and fluorenol in the presence of potassium *tert*-butoxide (Table XVIII) are in accord with a reaction involving initial ionization to a carbanion or dianion.

Consistent with the above conclusion is the observation that the ketyl of fluorenone is formed in nearly quantitative yield from a mixture of fluorenone and fluorenol in DMSO(80%)–*tert*-butyl alcohol(20%) in the presence of excess potassium *tert*-butoxide (*62, 63*). Appreciable concentrations of the ketyl were also formed under the reaction conditions in *tert*-butyl alcohol or pyridine solutions (*62, 63*). Similarly, the ketyl is readily prepared in these solvents by the reaction of a deficient quantity of oxygen with fluorenol in the presence of potassium *tert*-butoxide or by the action of bases on the pinacol (*62, 63*). The ketyl of xanthenone is readily prepared in pyridine or DMSO(80%)–*tert*-butyl alcohol(20%)

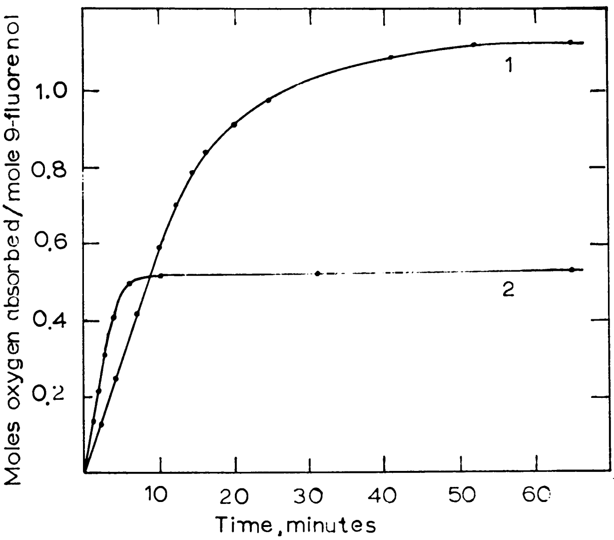


*Figure 20. Oxidation of 0.15*M *9-fluorenol in* tert-*butyl alcohol containing 0.39*M *potassium* tert-*butoxide; (1) no additive; (2) 0.002*M *$FeCl_3$*

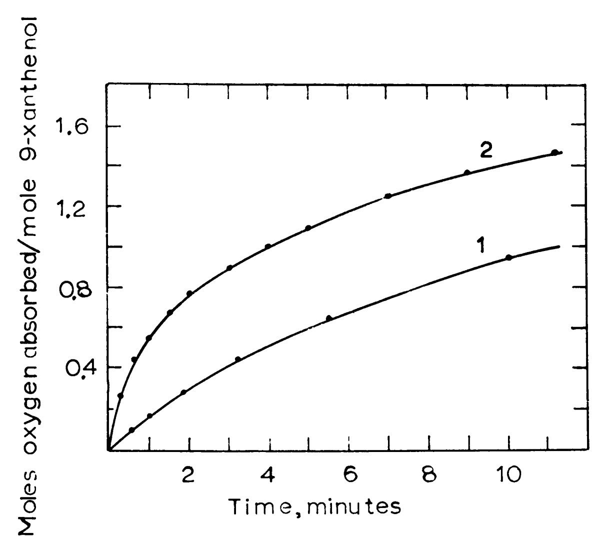


*Figure 21. Oxidation of 0.12*M *9-xanthenol in pyridine (80%)-*tert-*butyl alcohol (20%) containing 0.36*M *potassium* tert-*butoxide; (1) no additive; (2) 0.005*M p-*cyanonitrobenzene*

Table XVIII. Products of Oxidation of Fluorenol and Xanthenol[a]

Substrate (3 Mmoles)	*Solvent[b]*	*Base (9 Mmoles)*	*Oxygen Absorbed, Mmoles (min.)[c]*	*Products, %*
Xanthenol	*tert*-BuOH	$KOC(CH_3)_3$	3.2 (42)	Xanthenone, 99
Fluorenol	*tert*-BuOH	$KOC(CH_3)_3$	3.9 (42)	Fluorenone, 81
Xanthenol	Py	$KOC(CH_3)_3$	5.7 (62)	
Fluorenol	Py	$KOC(CH_3)_3$	6.3 (80)	
Xanthenol	DMSO	$KOC(CH_3)_3$	5.55 (27)	Xanthenone, 89
Fluorenol	DMSO	$KOC(CH_3)_3$	4.2 (35)	9-(methylsulfinylmethyl)-9-hydroxyfluorene, 72
Xanthenol	DMSO	$LiOC(CH_3)_3$	3.0 (12)	Xanthenone, 87
Fluorenol	DMSO	$LiOC(CH_3)_3$	2.9 (3)	Fluorenone, 71
Xanthenol	DMSO	$RbOC(CH_3)_3$	5.8 (43)	Xanthenone, 97
Fluorenol	DMSO	$RbOC(CH_3)_3$	4.3 (20)	
Xanthenol	Py	$RbOC(CH_3)_3$	5.1 (129)	Xanthenone, 96
Fluorenol	Py	$RbOC(CH_3)_3$	4.3 (8)	Fluorenone, 71
Xanthenol	DMSO	$NaOC(CH_3)_3$	4.1 (11)	Xanthenone, 95
7-Acenaphthenol	DMSO	$KOC(CH_3)_3$	8.0 (60)	1,8-naphthalic anhydride, 22

[a] 50 ml. of solvent except for *tert*-butyl alcohol where 25 ml. of solvent was employed.
[b] DMSO = DMSO (80%)-*tert*-BuOH (20%), Py = pyridine (80%)-*tert*-butyl alcohol (20%).
[c] For complete oxidation.

solutions in the presence of potassium *tert*-butoxide by the oxidation of xanthenol or by the reaction of xanthenol with xanthenone (*62, 63*).

Table XVIII summarizes the stoichiometry and yield of products in the oxidation of fluorenol and xanthenol in basic solutions. Table XVIII indicates that in the presence of lithium alkoxides that the reaction proceeds to give only lithium peroxide, but in the presence of the other alkali cations, particularly potassium and rubidium, the superoxide is a major product. In the oxidation summarized in line 5 of Table XVIII, 0.45 grams of potassium superoxide was recovered by filtration followed by thorough washing with the reaction solvent. Analysis by oxygen evolution indicated potassium superoxide with purity of 99%. Thus of the total 5.55 mmoles of oxygen absorbed, 5 mmoles were recovered in the form of potassium superoxide. The oxidation of xanthenol in the presence of rubidium *tert*-butoxide absorbed 1.92 mmoles of oxygen per mole of alcohol to yield an inorganic peroxidic precipitate which was hydrolyzed to rubidium hydroxide. Titration by acid indicated a composition of $RbO_{1.89}$ for the initial precipitate. The stabilities of the alkali metal superoxides are Rb,K > Na > Li (*73*). The tendency to form the superoxide in the oxidation of fluorenol or xanthenol apparently follows the stability of the superoxide. The data of Table XVIII indicate that at short reaction periods the ratio of inorganic peroxide to superoxide depends on the structure of the alcohol being oxidized. Since this is the case the mechanism for superoxide formation cannot be simply that of oxidation of the peroxide (K_2O_2) (*48, 49*). The best rationalization of the oxidation of fluorenol or xanthenol would appear to be the following scheme.

$$R_2CHOH \overset{B^-}{\rightleftharpoons} R_2CHO^- \overset{B^-}{\rightleftharpoons} R_2CO^{-2}$$

$$RaCO^{-2} + O_2 \rightarrow R_2CO\cdot^- + O_2\cdot^-$$

$$R_2CO\cdot^- + O_2 \rightarrow R_2CO + O_2\cdot^-$$

$$R_2CO^{-2} + O_2\cdot^- \rightarrow R_2CO\cdot^- + O_2^{-2}$$

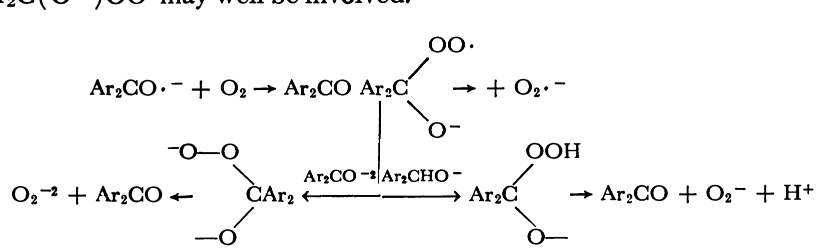
$$R_2CO\cdot^- + O_2\cdot^- \rightarrow R_2CO + O_2^{-2}$$

A radical-chain mechanism involving electron transfer reactions appears to present the best rationalization of the observations made in this study of the oxidation of diarylcarbinols. Under the reaction conditions employed it has been possible to discern two general courses for the oxidation of diarylcarbinols in basic solution. For benzhydrol and most benzyl alcohols the oxidation involves hydrogen abstraction from the alkoxide anion derived from the alcohol. For the more acidic fluorenol or xanthenol the oxidation appears to involve electron transfer from a carbanion or dianion intermediate to the attacking radicals. By choosing solvent and base it should be possible to switch from one mechanism to another with a given alcohol or to obtain situations wherein both alkoxide and carbanion intermediates are involved in the oxidation of xanthenol in *tert*-butyl alcohol containing potassium *tert*-butoxide.

The oxidations involving carbanion intermediates are readily catalyzed by reagents capable of one-electron oxidation, whereas the oxidations involving only alkoxide ions as intermediates are susceptible to inhibition by reagents which destroy intermediate chain-branching peroxides.

The oxidations of both benzhydrol and fluorenol involve ketyl radical-anions as intermediates which, in the presence of excess oxygen, yield both potassium superoxide and peroxide. The stoichiometry of the reaction in the solvents employed is complicated by the stabilization of potassium superoxide by precipitation in the form of an ill-defined complex with potassium *tert*-butoxide and by a slow, apparently heterogeneous oxidation of potassium peroxide to the superoxide.

The mechanism of electron transfer from the ketyl radical-anion to molecular oxygen has not been defined. An intermediate of the type, $Ar_2C(O^-)OO\cdot$ may well be involved.



However, we know of no evidence that requires this intermediate, and until such evidence is presented we prefer to picture the transfer of an

electron from the ketyl of an aromatic ketone to molecular oxygen as a one-step process involving only a collisional complex. Futhermore, we have argued previously that the formation of superoxide is not consistent with a peroxy radical mechanism owing to:

$$ROO\cdot + O_2\cdot^- \rightarrow RO_2^- + O_2$$

Experimental

General Oxidative Techniques. The autoxidations were performed using the wrist action shaker shown in Figure 22. Much better contact between oxygen and the liquid phase was obtained with this shaker than with paddle or stirring bar stirrers. The shaking motion in a creased flask

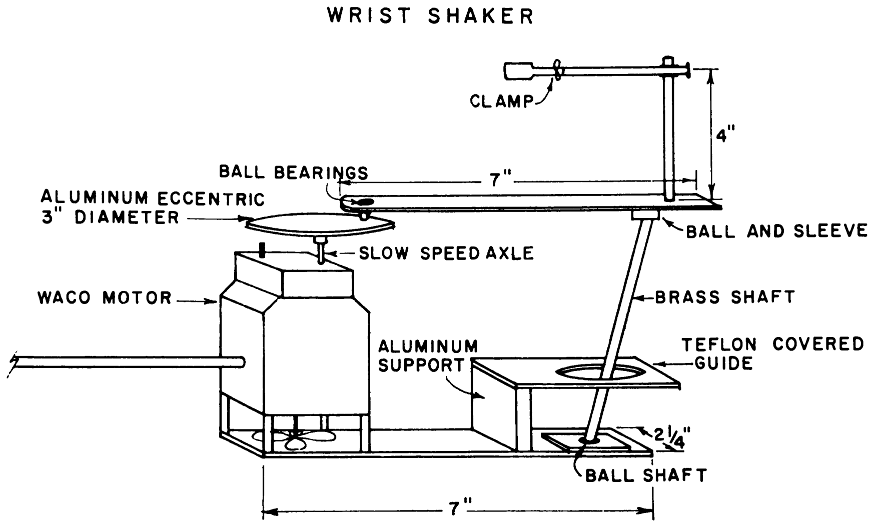


Figure 22. Wrist action shaker employed in oxidation studies

causes the solution to become frothy and provides excellent contact between a large liquid surface and gaseous oxygen. The oxidation flasks were 100–200 ml. creased flasks of the type shown in Figure 23. The flasks were connected by short lengths of Tygon tubing to a manifold containing an oxygen inlet valve, a pressure relief by-pass (mercury bubbler), a gas buret with a motor-driven mercury leveling bulb, a precise closed-end mercury or oil manometer, and a vacuum connection. Solutions of base were degassed in the flask by evacuation with cooling of the solvent if required. Oxygen was then introduced through the center tube extending below the surface of the solution (Figure 23). To insure saturation of the basic solution, oxygen was then allowed to bubble through the solution and escape through the three-way stopcock in the by-pass to the center tube. For more exact temperature control the whole

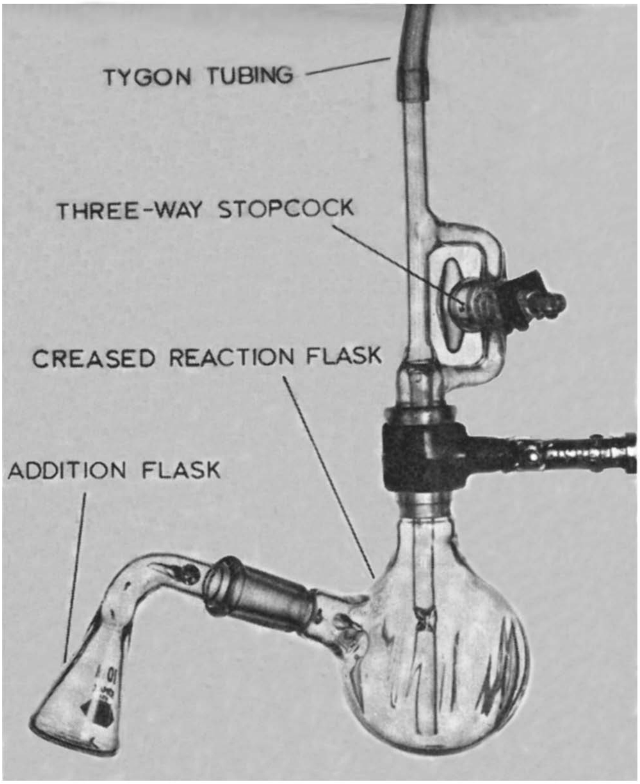


Figure 23. Oxidation flask with addition sidearm

flask was immersed in a thermostated water bath from 20 minutes prior to the start of the oxidation reaction. For the actual oxidation the flask was removed from the thermostating bath, attached to the wrist action shaker, and the three-way stopcock adjusted by a mercury leveling bulb. The material to be oxidized was then added to the flask as a solid, liquid, or solution by turning the retort-shaped addition flask (Figure 23) and the shaker immediately started. For the slower oxidations automatic control of the mercury leveling bulb was achieved by a simple device described elsewhere (*43*).

Our early work in this area utilized a vigorously shaken flask mounted on a motor-driven rack in a thermostated bath (*61*). Although excellent agitation and temperature control can be achieved in this manner, it is difficult to introduce the compound to be oxidized to an oxygen-saturated solution of the base. Three methods of agitation in the autoxidation of 2-nitropropane in aqueous solution are compared in Figure 24. Excellent agreement was obtained between the results observed utilizing the motor-driven shaking rack and the wrist-action shaker. A magnetic stirring bar developing a well defined vortex with some foaming failed to give a pronounced autocatalytic reaction (Figure 24) as was observed with the other two methods of stirring, apparently because of a lowered rate of diffusion of oxygen into the solution.

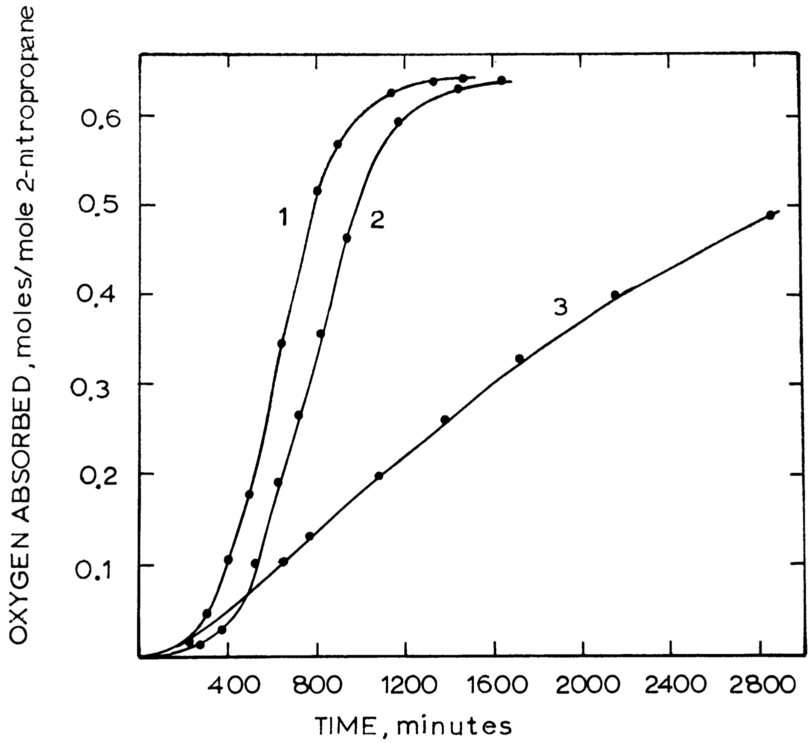


*Figure 24. Oxidation of 0.1*M *2-nitropropane in 1.5*M *aqueous sodium hydroxide solution; (1) variable speed reciprocating rack, (ref. 61); (2) wrist-action shaker; (3) magnetic stirring bar*

Electron Spin Resonance Measurements. A Varian V-4500 spectrometer (~ 9.5 Gc./s.) equipped with 100 kc./s. field modulation was employed in conjunction with flat fused silica cells ("aqueous sample cell"). The two most common experimental arrangements are shown in Figures 25 and 26. The inverted U-cell arrangement of Figure 25 provided for solutions of a base and of an organic material or mixture of materials to be introduced into separate legs of the cell. Prepurified nitrogen was bubbled through these solutions by means of stainless steel hypodermic needles inserted through the rubber septums. After deoxygenation was complete (10–20 minutes) the hypodermic needles were removed, the silica ESR cell stoppered, and the solutions mixed without contacting the rubber septums. The mixed solution was then shaken down with the ESR cell. Spectra could be recorded within about 1 minute of mixing. The deoxygenated solutions could also be exposed to traces of air by removing the silica ESR cell for a period of 10–30 seconds before shaking the solution down into the silica cell. For some experiments the inverted-U mixing cell was fitted with ground glass closures and the fused silica cell attached to a vacuum system. The apparatus was deoxygenated by freeze-thawing and finally filled with helium. The apparatus was re-

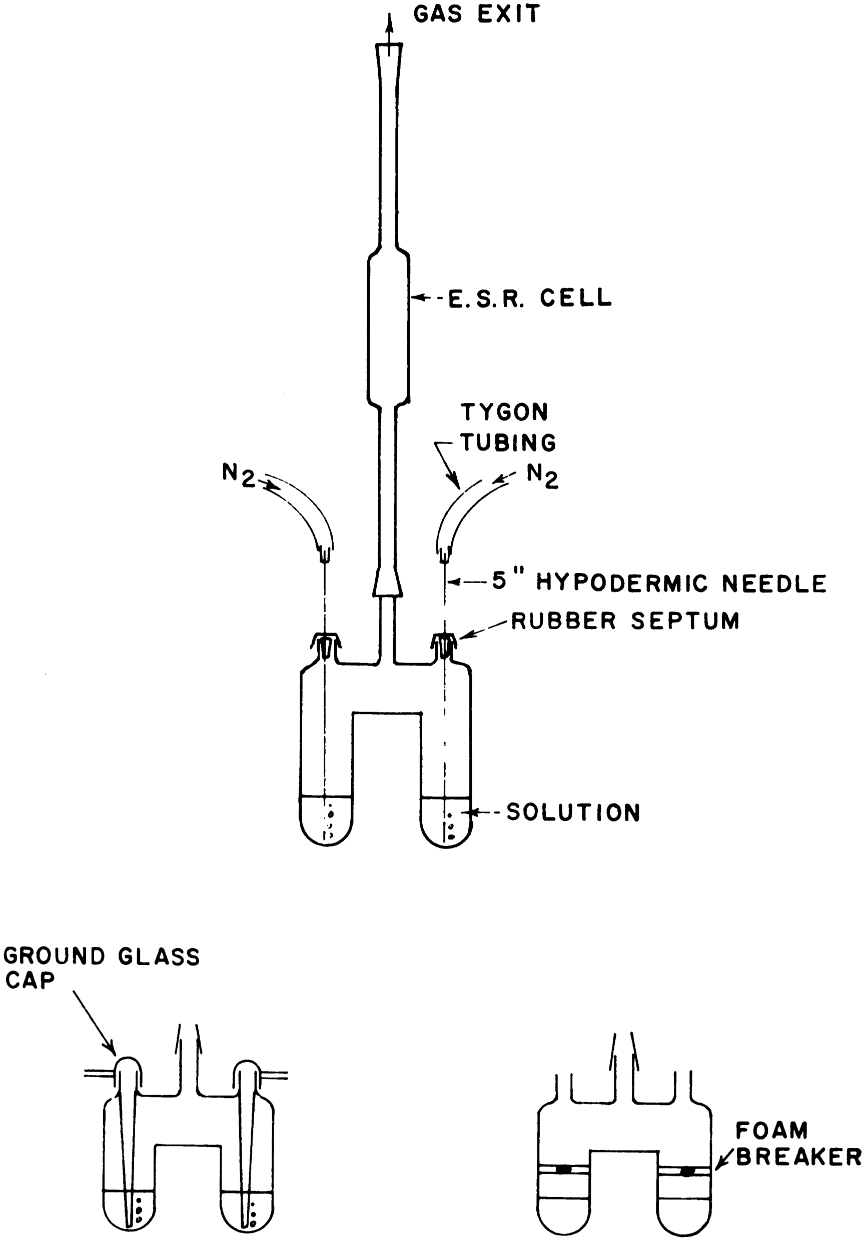


Figure 25. Inverted U-cell for electron spin resonance measurements

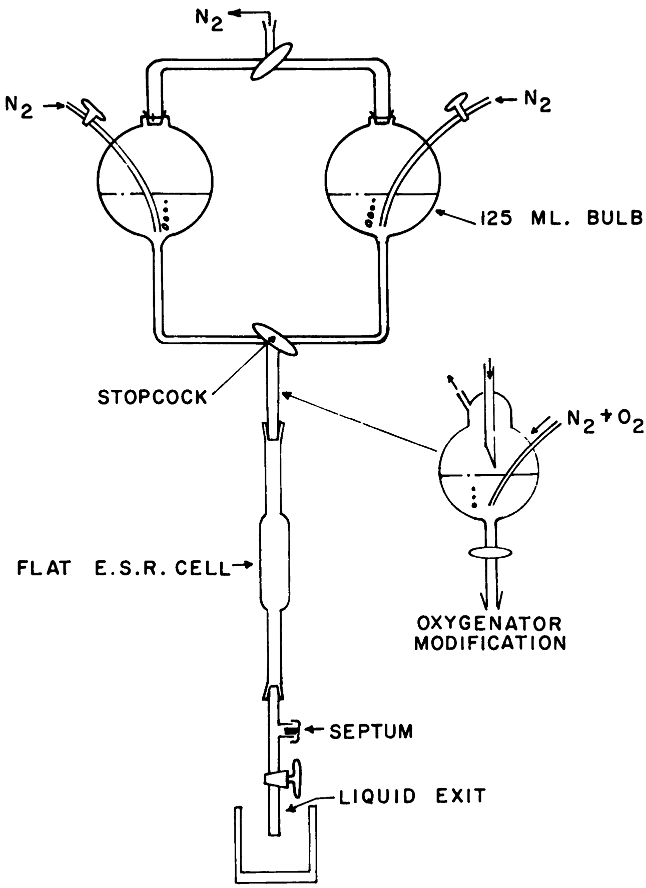


Figure 26. Flow system for electron spin resonance experiments

moved from the vacuum line and stoppered before the solutions were mixed and introduced into the fused silica cell.

For more rapid electron-transfer experiments the flow system of Figure 26 was employed. This involved two or three liquid reservoirs containing (1) a solution of base, (2) a solution of an organic compound or mixture of compounds, and (3) solvent. The solutions were thoroughly deoxygenated by a stream of prepurified nitrogen. Solutions 1 and 2 were mixed, usually at a 1:1 ratio, under a positive pressure at a three-way Teflon stopcock and allowed to flow through the flat fused-silica ESR cell. Flow times between mixing and radical detection were easily varied between 1 minute and 0.3 seconds. Radical-anions were either detected during flow (steady state concentrations) or during the period after the flow had been stopped. In a modified arrangement (Figure 26) the surface of the deoxygenated final solution could be exposed to a controlled partial pressure of oxygen for a short period of time before flowing into the ESR cell.

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